REGISTERED NO. M. 3121

PHYSICS LIBRARY

PROCEEDINGS

OF THE

INDIAN ACADEMY

OF SCIENCES

VOL. XXXIV] *SECTION A* [NO. 2

AUGUST, 1951

Price Rs. 2 or 3 Sh. *Annual Subscription Rs. 18*

PRINTED AT THE BANGALORE PRESS, BANGALORE CITY, BY G. SRINIVASA RAO, SUPERINTENDENT, AND PUBLISHED BY THE INDIAN ACADEMY OF SCIENCES, BANGALORE.

THE SCATTERING OF LIGHT IN CRYSTALS AND THE NATURE OF THEIR VIBRATION SPECTRA

By Sir C. V. Raman

(From the Raman Research Institute, Bangalore)

Received August 3, 1951

1. Introduction

In an essay[1] by the present writer published in February 1922, it was remarked that transparent crystals, such as ice and quartz, when traversed by an intense beam of white light, exhibit an observable blue opalescence due to the diffusion of the incident radiations by the thermally induced fluctuations of density and refractive index in the medium. Six years later,[2] the use of monochromatic light and of spectral analysis in such studies revealed that in the radiations scattered by crystals, there are large and readily observable shifts of frequency. The field of investigation opened up in 1922 was thus vastly enlarged by the discovery of 1928. Since that time, many investigations have been made and much valuable knowledge gathered regarding the scattering of light in crystals and the accompanying changes of frequency.

In any attempt to connect the physical properties of crystals with their ultimate structure, we inevitably come up against the following questions. What is the nature of their vibration spectra, and how are the modes and frequencies of vibration of the atoms in a crystal related to its structure? The answers to these questions are of fundamental importance to the physics of the solid state. The study of the spectral shifts observed in light scattering is the most powerful method available to us for obtaining information concerning these issues. It is the purpose of the present paper to show that a consideration of the facts ascertained by such studies enables us to reach definite conclusions regarding the questions raised above.

2. The Two Types of Light Scattering in Crystals

Spectroscopic studies have shown that the scattering of light in crystals is of two distinct species which differ fundamentally in their observable characters and which correspond respectively to the two phenomena whose existence was recognised in 1922 and in 1928. The first type of light-scattering is an effect primarily of thermal origin: the frequency shifts in it vary with the angle of scattering and are so small that they can only be

measured with the most powerful instrumental aids at our disposal. Quantitative studies of this type of scattering have shown that it arises from the presence in the crystal of sound-wave patterns of thermal origin which diffract the light-waves traversing it. In other words, the light-scattering of the first kind is a macroscopic phenomenon which can be explained in purely classical fashion. The second type of light-scattering differs from the first in the magnitude of the frequency shifts which are much larger and correspond to wave-lengths in the infra-red spectrum. From this and the fact that similar effects are also observed with other states of molecular aggregation, *viz.*, gases, liquids and amorphous solids, we infer that the second type of light-scattering, unlike the first, is a molecular phenomenon which is explicable only on quantum-mechanical principles. This conclusion is confirmed by many other facts of observation and especially by the results of comparative studies made with materials in diverse states of molecular aggregation. Such studies enable us to understand how the state of aggregation influences the observed phenomena and assist us in reaching a correct interpretation of the effects observed with crystals.

3. The Elastic Vibrations of Crystalline Solids

The spectral shifts of frequency observed in the scattering of light by gases are of three distinct species and of widely different orders of magnitude which we associate respectively with the three possible kinds of movement of a free molecule, *viz.*, translation, rotation and vibration. Likewise, in the case of crystals, we shall be justified in assuming that the two types of light-scattering actually observed are associated respectively with the two possible kinds of movement of the lattice cells of a crystal, *viz.*, translations and internal vibrations. The translatory movements have no pre-determined frequency of their own, whereas the internal vibrations may clearly be expected to possess characteristic frequencies fixed by the structure of the crystal, *viz.*, by the masses and positions of the atoms and the strength of the interatomic forces. It is thus evident that the two classes of movement differ fundamentally in their nature and they have therefore to be considered separately.

The translatory movements of the lattice cells may properly be identified with the displacements of the volume-elements in the crystal contemplated in the classical theory of elastic wave-propagation in solids. The whole of that theory is based on the assumption that a solid may be subdivided into volume elements small enough to justify their being treated as single particles for the evaluation of their kinetic energy and yet large enough for the potential energy of deformation to be evaluated on the same basis as

for a solid of macroscopic dimensions. The assumption is a justifiable approximation, provided the wave-length of the elastic vibration is large compared with the lattice spacings of the crystal and its frequency is small in comparison with the characteristic frequencies of its structure. But as we go down in the scale of wave-lengths or go up in the scale of frequencies, we would inevitably reach and pass the limits beyond which these are no longer valid assumptions. It follows that the ideas and methods of the classical theory of elasticity are limited in their application to the movements in the lower ranges of frequency where the elastic displacements may properly be identified with translatory movements of the lattice cells of the crystal, and only infinitesimal alterations in the interatomic distances are involved. The situation is entirely different in the second class of movements, *viz.*, the internal vibrations of the lattice cells which we now proceed to consider.

4. The Characteristic Vibrations of Crystal Structures

The vibrations of a free polyatomic molecule and the internal vibrations in the lattice cells of a crystal differ in so far as that in the latter case, the interactions between each unit of the structure and those surrounding it have to be considered. The results of such interaction can be foreseen by considering the simple example of two pendulums of equal length suspended from a common support. The yielding of the support and the consequent coupling of the pendulums results in the system having two different periods of oscillation instead of one; the oscillations of the two pendulums have equal amplitudes in both cases, but their phases are the same in one case and opposite in the other. In a paper published eight years ago in these *Proceedings*,[3] the writer gave a formal proof of the following theorem which is the generalised three-dimensional analogue of the theory of coupled oscillators. *In the normal modes of vibration of the structure of a crystal, equivalent atoms in adjacent cells have the same amplitude of vibration, while their phases are either the same or else opposite in successive cells of the lattice along each of its three axes.* An easy verification of this theorem is furnished by considering the effect of giving the crystal a unit displacement along any one of the three axes of the lattice. Such displacement brings the atoms in a cell into the positions previously occupied by the equivalent atoms in an adjacent cell: since the normal mode is a characteristic property of the crystal structure, we should expect it to remain unaltered following the unit translation, and it is readily seen that this is so in all the cases covered by the theorem and *in no others*. In other words, the theorem provides us with a means of completely enumerating the possible normal modes of vibration of the structure of the crystal.

Since the phases of the vibration of equivalent atoms in adjacent cells may be either the same or opposite along each of the three axes of the lattice structure, we have $2 \times 2 \times 2$ or 8 distinct situations regarding the relative phases of the vibrations in a unit cell and in those surrounding it. Thus, when we proceed to write down the $3p$ equations of motion of the p atoms in a unit cell, taking into account the interactions with the atoms in surrounding cells, we have to consider 8 different sets of $3p$ equations, each of which contains $3p$ variables. Accordingly, we obtain $24p$ solutions in all. This total number may be subdivided as follows: $(3p - 3)$ solutions represent normal modes of vibration in which the phases are the same in adjacent cells of the structure; $21p$ solutions represent normal modes in which the phases of vibration are opposite in adjacent cells along one, two or all three of the axes of the lattice; and finally a residue of 3 solutions which represents the three excluded translations. An element of volume whose dimensions are twice as large and whose content is therefore 8 times as great as for a unit cell of the crystal, would contain $8p$ atoms whose total degrees of freedom would number $24p$. The $(24p - 3)$ normal modes of vibration indicated by the theory may therefore be regarded as the modes of internal vibration of the atoms included in this 8-cell unit, and the 3 excluded solutions as the three translations of such unit.

5. The Nature of the Vibration Spectrum

The results of the two preceding sections may be summed up by the statement that the character of the vibration spectrum is totally different in the two regions of it arising respectively from the translations and vibrations of the lattice cells of the crystal. The translatory movements give us a continuous spectrum of elastic vibrations lying in the lower range of frequencies, while the vibratory movements give us a line-spectrum which is characteristic for the crystal and appears in the upper or infra-red range of frequencies. The total degrees of freedom of atomic movement in the crystal are divided between the two species of vibration in the proportion of $(24p - 3) : 3$. Thus, even in crystals with the simplest structures for which $p = 1$, only one-eighth of the total degrees of freedom appears as vibrations of the elastic solid type. For crystals with more complex structures for which $p = 2$ or 3 or any larger number, the proportion is correspondingly smaller and the vast majority of the degrees of freedom appear as the characteristic modes of vibration of the crystal structure.

The foregoing results enable us without further explanation to understand the phenomena exhibited by crystals in light-scattering. It is known that the frequency shifts exhibited by crystals appear, in general, as sharply

defined lines. They evidently owe their origin to the activity in light-scattering of one or more of the $(3p - 3)$ characteristic modes of vibration in which the phase is the same in adjacent cells: the remaining $21p$ modes are necessarily inactive, since their vibrations alternate in phase along one or more of the axes of the lattice. The number of frequency shifts actually observed in any case may be fewer than $(3p - 3)$. For, as a consequence of the symmetry properties of the crystal, some of the $(3p - 3)$ modes may have the same frequency and the number of distinct frequencies would thereby be reduced. Again, some of the $(3p - 3)$ modes might be inactive by reason of their being of an antisymmetric type.

The continuous spectrum of elastic vibrations would necessarily be inactive in light-scattering, since the phase alternates in successive cells of the stationary wave-pattern. An exception, however, arises when the separation between the nodal planes of the pattern is so related to the wavelength of the light traversing the crystal and the angle of incidence on the nodal planes that there is a coherent reflection of the incident light waves by the elastic wave pattern. Such a reflection would exhibit frequency shifts, both positive and negative, the magnitude of which depends on the angle of scattering, as is actually observed.

6. Overtones and Combinations

The so-called second-order spectra of light-scattering are very feeble and can only be recorded under intense excitation. They appear when the amplitudes of atomic vibration in any particular mode or modes are finite in comparison with the interatomic distances. For, in such a case, the anharmonicity of the optical polarisability would result in the scattered radiations including spectral components whose frequency shifts are overtones and summations of the vibration frequencies of the modes under consideration.

It is evident that the thermally excited vibrations of the elastic solid type would be incapable of giving any observable second-order effects. For, the energy of any such vibration having a specified frequency would be distributed over the volume of the crystal and the amplitudes of vibration could, therefore, only be infinitesimal. The interatomic displacements associated with the translatory movements would be of a still smaller order of magnitude. Hence, the local variations in optical polarisability associated with the elastic vibration of any particular frequency would be excessively small, and since they vary in phase from point to point within the crystal, their external effects would cancel out completely. In other

words, the elastic vibrations of all frequencies are inactive in light-scattering not merely in the first approximation, but absolutely, except in the particular case of a coherent reflection already referred to. Even in this case, there could be a first-order effect but none of higher order.

The situation is altogether different in the case of the characteristic vibrations whose frequencies lie in the infra-red range. The excitation of these vibrations is a quantum-mechanical effect, and the energy of excitation would necessarily be localised in the element of volume under consideration, *viz.*, a group of lattice cells whose linear dimensions are of the same order of magnitude as the range of the intermolecular forces. A quantum of vibrational energy when distributed over such a small volume would result in atomic movements of finite amplitudes and hence, as the result of optical anharmonicity, give rise to scattered radiations with overtones or summational frequency-shifts.

The second-order spectra arising in the manner explained could include overtones and summations of the frequencies of all the $(24p - 3)$ modes and not merely of those modes which are active in the first order. The $21p$ modes which are inactive in the first approximation may thus become accessible to observation, though only as overtones or summations. The second-order spectrum of light-scattering would necessarily be a line spectrum. But as the overtones and summations would be numerous, it would be a crowded spectrum, and further crowding up may arise from subsidiary effects, such as a splitting up of individual overtones or summations into several distinct components as the result of mechanical anharmonicity and removal of degeneracy. We cannot, therefore, expect the line character of the second-order spectrum to be quite so obvious to inspection in all cases as with the spectrum of the first order.

7. The Theoretical Conclusions

We may now sum up the conclusions reached in the preceding sections.

I. The frequencies of characteristic vibration of the structure of a crystal constitute a line spectrum. This is accompanied by a continuous spectrum of elastic vibrations in the lower ranges of frequency. Only 3 out of every $24p$ degrees of freedom appear in the latter.

II. The $(3p - 3)$ characteristic modes in which the phase of the vibration is the same in adjoining cells of the structure may appear as frequency shifts in light-scattering: the $21p$ modes in which the phase alternates along one, two or all the three axes of the lattice are inactive.

III. Overtones and summations of the frequencies of all the $(24p - 3)$ modes are, however, allowed as frequency shifts in light-scattering.

IV. The continuous spectrum of elastic vibrations is inactive in light-scattering except in the particular case of a coherent reflection of the light-waves by the elastic wave-patterns. Overtones and summations of their frequencies are totally forbidden.

8. Some Illustrative Examples

(i) *Diamond* (Fig. 5 in Plate V and Figs. 6 and 7 in Plate VI).—The simplicity of the structure of diamond and its cubic symmetry enable its characteristic modes of vibration to be completely described and their frequencies to be evaluated by a rigorous procedure. The $(24p-3)$ or 45 modes possible give only 8 distinct frequencies. Expressed in wave-numbers, they are, 1332 (3), 1250 (8), 1232 (6), 1149 (4), 1088 (6), 1008 (4), 752 (6) and 620 (8), the numbers enclosed in brackets being their respective degeneracies. The first or triply degenerate mode represents an oscillation having the same phase in adjacent cells of the lattice, while the others are modes in which the motion alternates in phase in successive cells. The three elastic constants of diamond can also be computed theoretically from the same set of force-constants as the characteristic vibration-frequencies and used to evaluate the distribution of frequency in the continuous spectrum of elastic vibrations. Thus, all the data necessary are forthcoming for an independent calculation of the specific heats of diamond. A satisfactory agreement is found between the calculated and observed elastic constants, as also between the calculated and observed specific heats over the whole range of temperature for which data are available.

That diamond exhibits a single sharp and intense line with a frequency shift of 1332 cm.$^{-1}$ in light-scattering was discovered by C. Ramaswamy in the year 1930. More recent investigations by R. S. Krishnan revealed the second-order spectrum with all the features predicted by the theory. Likewise, it was shown by him that the continuous spectrum of elastic vibrations is completely inactive in light-scattering except in the particular case of a coherent reflection of the incident light-waves by the elastic wave-pattern.

The case of diamond thus affords a complete quantitative verification of the theoretical conclusions set forth above. The reader is referred to recent papers by P. S. Narayanan[4] and D. Krishnamurti[5, 6] in these *Proceedings* for further details of the case and for literature citations.

(ii) *α-Quartz* [Figs. 8 (*a*) to (*d*) in Plate VII].—The three atoms of silicon and six of oxygen in each unit cell of the structure of quartz give us

($3p - 3$) or 24 modes of vibration having identical phases in adjoining cells. The trigonal symmetry reduces this number to 16 distinct frequencies and renders 4 of them inactive in light-scattering. Thus, only 12 frequency shifts are to be expected in the first-order spectrum. This is the number actually recorded in moderately exposed spetrograms, provided two rather close doublets actually observed are counted as single lines. If all the ($24p - 3$) or 213 fundamental frequencies of vibration of the structure could give octaves and summations with observable intensity, the second-order spectrum would obviously be very complex and difficult to decipher. Actually, by giving exposures about a hundred times greater than that necessary to record the first-order spectrum, R. S. Krishnan[7] obtained spectrograms which revealed 29 frequency shifts of the second-order. Only 17 of these could be explained as octaves and summations of the ($3p - 3$) modes, and the remaining 12 therefore presumably represent the strongest amongst the numerous others which are theoretically possible.

(iii) *Calcite and Aragonite* [Fig. 9 (*a*) and (*b*) in Plate VII].—Since there are two $CaCO_3$ groups in each unit cell of the calcite structure, the ($3p - 3$) characteristic modes of vibration in which the phase is the same in adjacent cell number 27 in all. The trigonal symmetry of the crystal reduces the number of distinct frequencies to 18, of which no less than 13 are inactive in light-scattering, leaving us with only 5 distinct frequency shifts to be expected in the first-order spectrum. Exposures about 500 times more prolonged than that sufficient to exhibit the first-order frequency shifts enabled R. S. Krishnan[8] to record 11 additional frequency shifts which could all be explained as overtones and combinations of the ($3p - 3$) characteristic frequencies of the structure.

Likewise, in the case of aragonite, R. S. Krishnan[9] obtained spectrograms exhibiting 25 frequency-shifts, 19 of which were fundamental frequencies and 6 belonged to the second-order spectrum.

(iv) *Barytes and Gypsum* [Fig. 10 (*a*), (*b*), (*c*), (*d*) in Plate VIII].—Strongly exposed spectrograms obtained with a large clear block of barytes and a high-speed instrument enabled R. S. Krishnan[10] to record no fewer than 39 frequency shifts with this crystal. 20 of these which were sufficiently intense to appear on spectrograms obtained with a much slower instrument were interpreted as first-order frequencies, and the remaining 19 (with one exception) as octaves and summations of them.

Likewise, in the case of gypsum,[11] 34 frequency shifts were recorded of which 29 were identified as belobging to the first-order spectrum and 5 as octaves and summational frequencies.

(v) *The Alkali Halides* [Fig. 11 (*a*) and (*b*) in Plate VIII].—By reason of the cubic symmetry of the structure of rock-salt, the $(24p - 3)$ or 45 possible modes of its vibration give only 9 distinct frequencies. As each metallic ion is surrounded symmetrically by six halogen ions and *vice-versa*, the triply-degenerate oscillation of the two sets of atoms against each other is inactive and there is, therefore, no first-order spectrum of light-scattering. The total number of octaves and summations which could appear in the second-order spectrum is 45, and since the fundamental frequencies are themselves degenerate in different degrees, mechanical anharmonicity would result in the splitting up of the summational frequencies into several distinct components. Hence, the second-order spectrum of the alkali halides would necessarily be rather complex, and the difficulty of exhibiting its discreteness or line-character would be enhanced by the fact that the entire spectrum falls within a range of 350 wave-numbers in the case of rock-salt and of 300 wave-numbers in the case of potassium bromide. Even so, the fact that some of the lines are much more intense than the rest, *e.g.*, 235 cm.$^{-1}$ in the case of rock-salt, makes the true nature of the spectrum evident to inspection, and it becomes even clearer when the spectrograms recorded by R. S. Krishnan[12] with instruments of lower and higher dispersing powers are compared with each other.

9. Descriptive Notes on the Spectrograms

The majority of the spectrograms illustrating this paper were obtained by Dr. R. S. Krishnan in the investigations already referred to. A few are by other authors (T. M. K. Nedungadi, P. S. Narayanan, M. M. Patel, V. M. Padmanabhan and Roop Kishore). All except those in Plate III were obtained with the intense excitation provided by the λ 2537 radiations of a water-cooled magnet-controlled mercury arc in quartz. The spectrograms have been reproduced as negatives for the sake of clarity.

Plate III, Figs. 1 *and* 2.—The spectrograms of naphthalene (crystal), benzophenone (both as liquid and as crystal) and of methyl methacrylate (glass) appearing in these figures illustrate the close similarity of the spectroscopic behaviour of liquids, amorphous solids and crystals in the region of higher frequencies. In all these cases, the larger frequency shifts are seen as sharp lines.

Plate IV, Figs. 3 *and* 4.—This series of six spectrograms illustrates the sharpness of the spectral shifts given with crystals and the increase in their number with increasing complexity of crystal structure. Fluorite gives only one frequency shift, while alumina gives 7, beryllium silicate 25, topaz 32,

Rochelle-salt 49, and cane-sugar 63 distinct frequency shifts. The mercury lines have been marked off with the symbol λ in the spectrograms to distinguish them from the frequency shifts given by the crystal.

Plate V, Fig. 5 *and Plate VI, Figs.* 6 *and* 7.—These illustrate the case of diamond. The development of a second-order spectrum in the region of frequency shifts between 2666 and 2176 with increasing exposures and its absence in the region of the elastic wave-spectrum even in heavily exposed spectrograms will be seen from Fig. 5 (*a*), (*b*) and (*c*). The microphotometer record in Fig. 6 and the high-resolution spectrograms in Fig. 7 exhibit very clearly the sharp lines with frequency shifts 2666, 2440–70 and 2176 which are the octaves of the fundamental frequencies 1332, 1232 and 1088 respectively.

Plate VII, Fig. 8.—This series of four spectrograms illustrates the development of the second-order spectrum of quartz with increasing exposures.

Plate VII, Figs. 9 (*a*) *and* (*b*).—These illustrate respectively the spectra of aragonite and calcite which are seen to be strikingly different. Some of the sharply defined lines appearing in the second-order spectrum of calcite are marked in Fig. 9 (*b*).

Plate VIII, Fig. 10 (*c*) *and* (*d*) illustrate strongly exposed spectra of barytes. Its second-order spectrum is clearly seen in both figures, but better in the more heavily exposed spectrogram.

Plate VIII, Figs. 11 (*a*) *and* (*b*).—Note the sharply-defined line with a frequency shift 235 seen in the second-order spectrum of rock-salt and the intense line with the frequency shift 126 in that of potassium bromide.

10. Summary

The facts of light-scattering in crystals are reviewed and the nature of the atomic movements and the character of their vibration spectra in the different frequency regions are deduced therefrom. Whereas the movements based on the translations of the lattice cells result in elastic wave motions in the solid with a continuous frequency spectrum, the modes based on their internal vibrations are localised and have monochromatic frequencies analogous to those of polyatomic molecules. The total degrees of atomic freedom are shared between the latter and the former in the ratio $(24p - 3) : 3$. The frequency shifts ordinarily observed in light-scattering arise from the group of $(3p - 3)$ modes in which the phase of the vibration is the same in adjacent cells of the lattice. But these as well as the $21p$ additional modes in which the phase alternates along the axes can give rise to shifts which are overtones and summations of their fundamental frequencies.

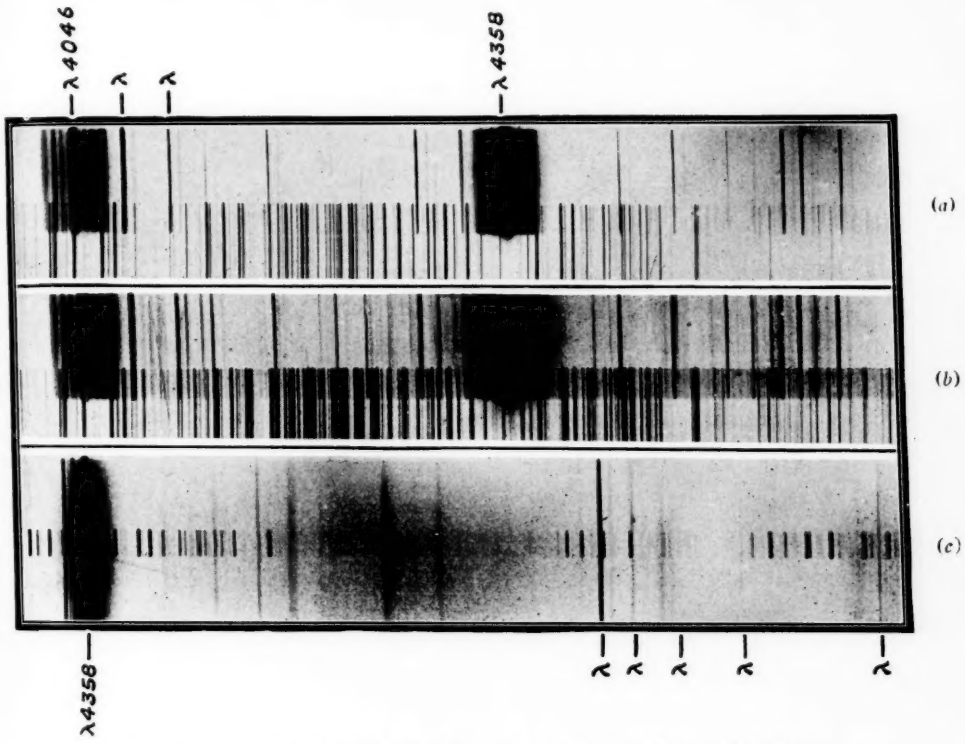


FIG. 1. (*a*) and (*b*): Naphthalene Crystals. (*c*): Methyl Methacrylate Glass

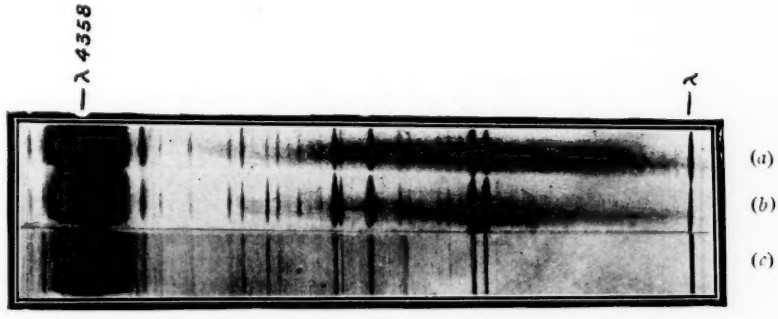


FIG. 2. (*a*) and (*b*): Benzophenone Liquid. (*c*): Benzophenone Crystal

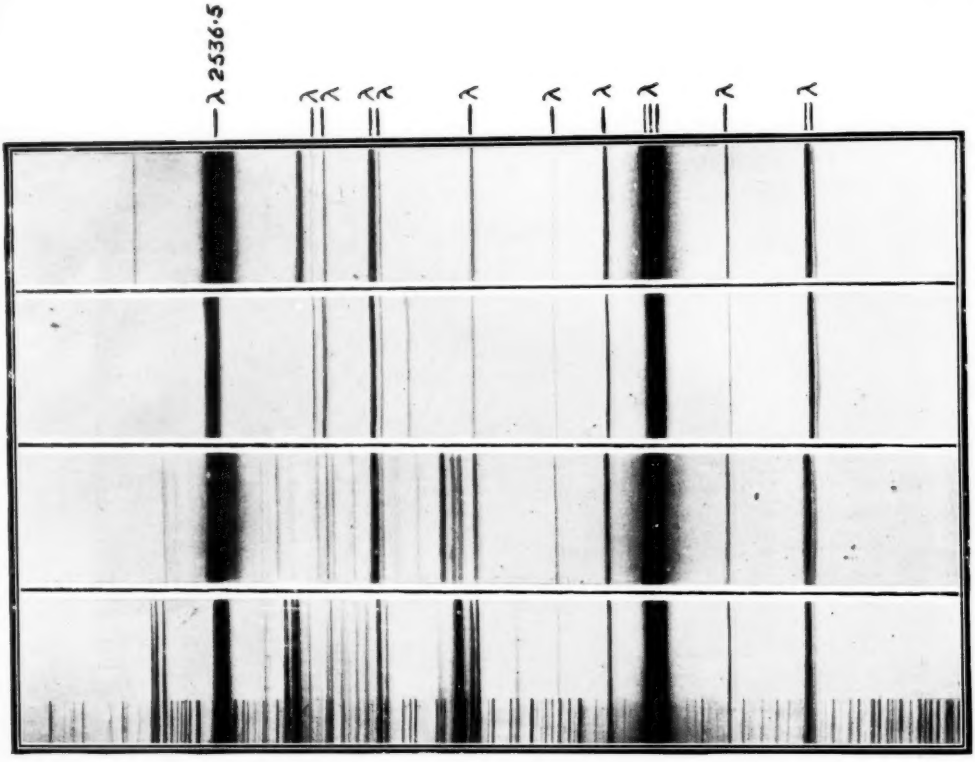


FIG. 3. (*a*) Fluorite. (*b*) Alumina. (*c*) Beryllium Silicate. (*d*) Topaz.

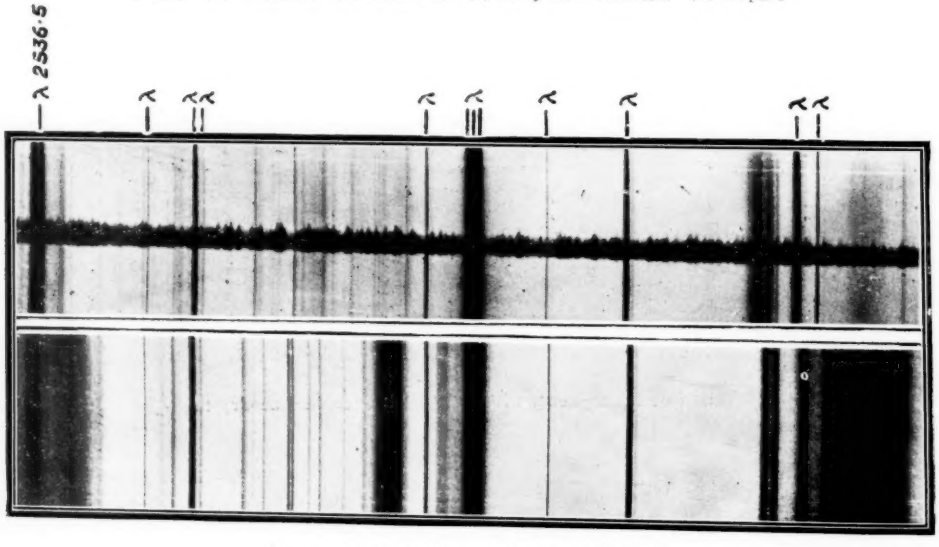


FIG. 4. (*a*) Cane-Sugar. (*b*) Rochelle Salt.

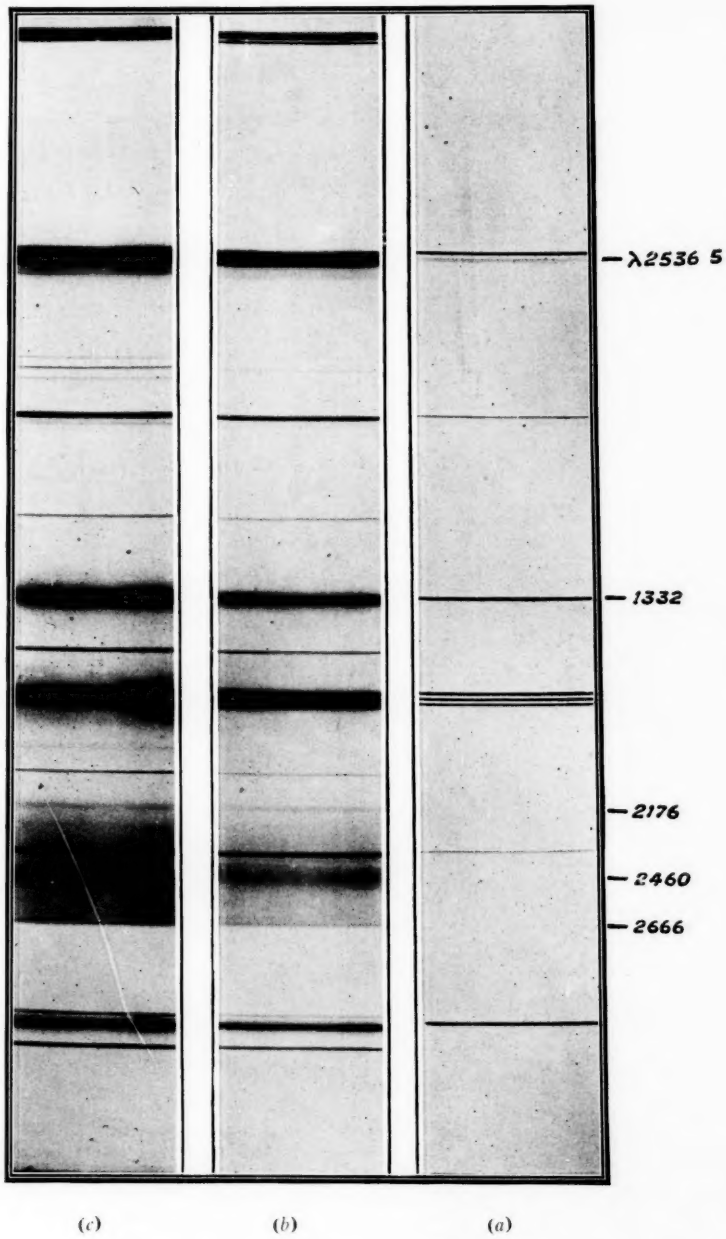


FIG. 5. Diamond (iMedum Spectrograph) (*a*), (*b*), (*c*) with increasing exposures

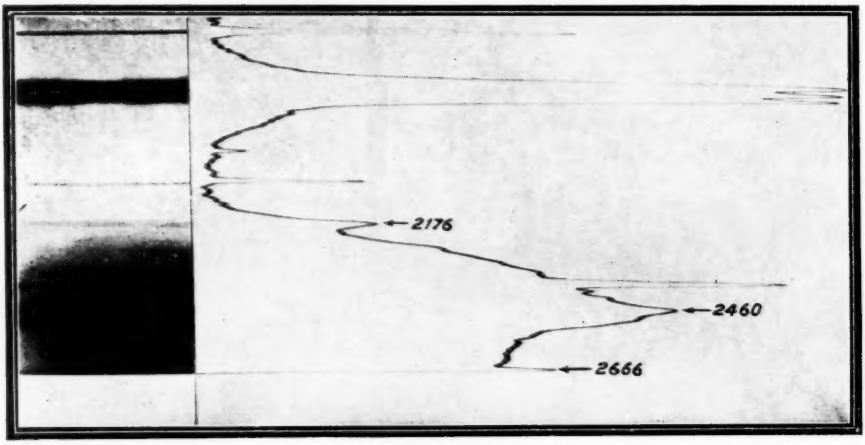


FIG. 6. Diamond (Medium Spectrograph)

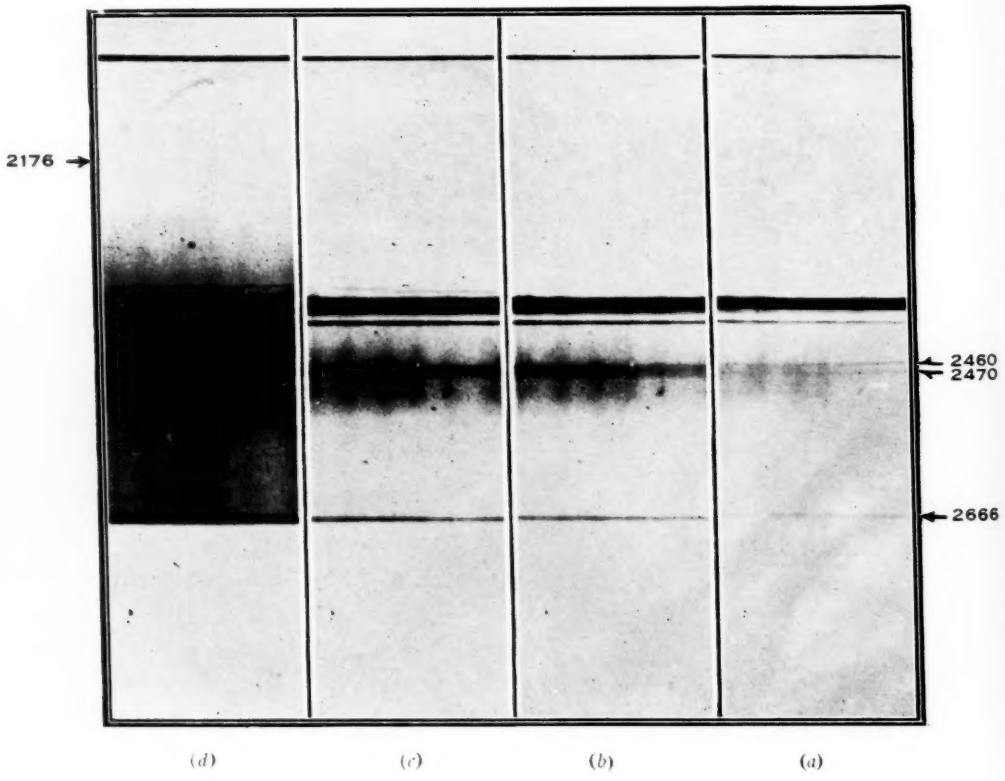


FIG. 7. Diamond (Large Spectrograph) (*a*), (*b*), (*c*), (*d*) with increasing exposures

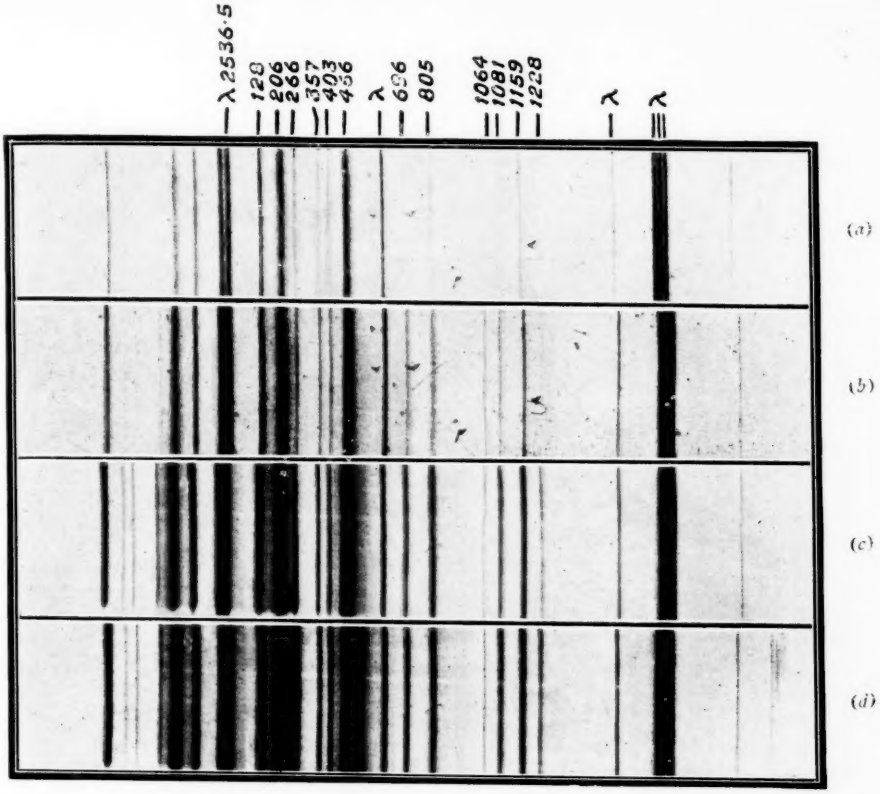


FIG. 8. Quartz: *a*), *(b)*, *(c)*, *(d)* with increasing exposures

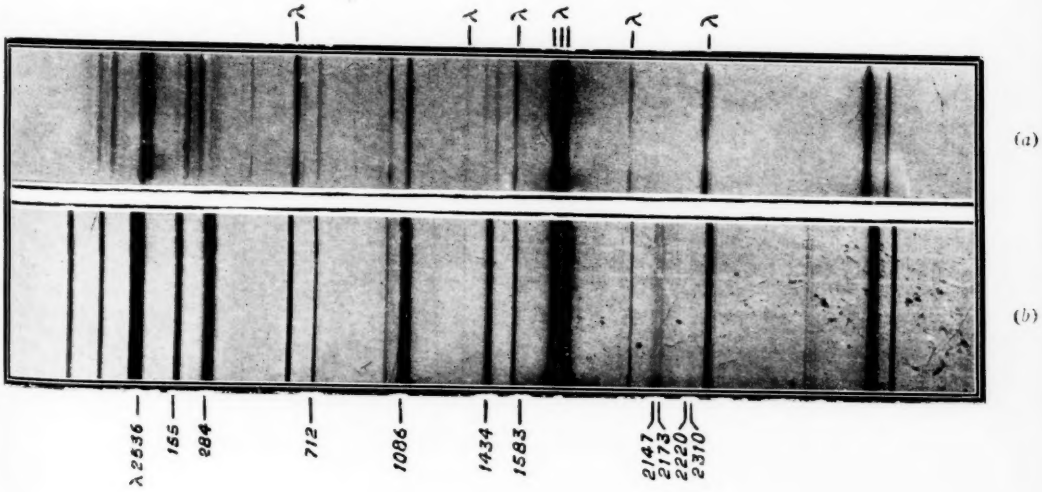


FIG. 9. *(a)*, Aragonite. *(b)* Calcite

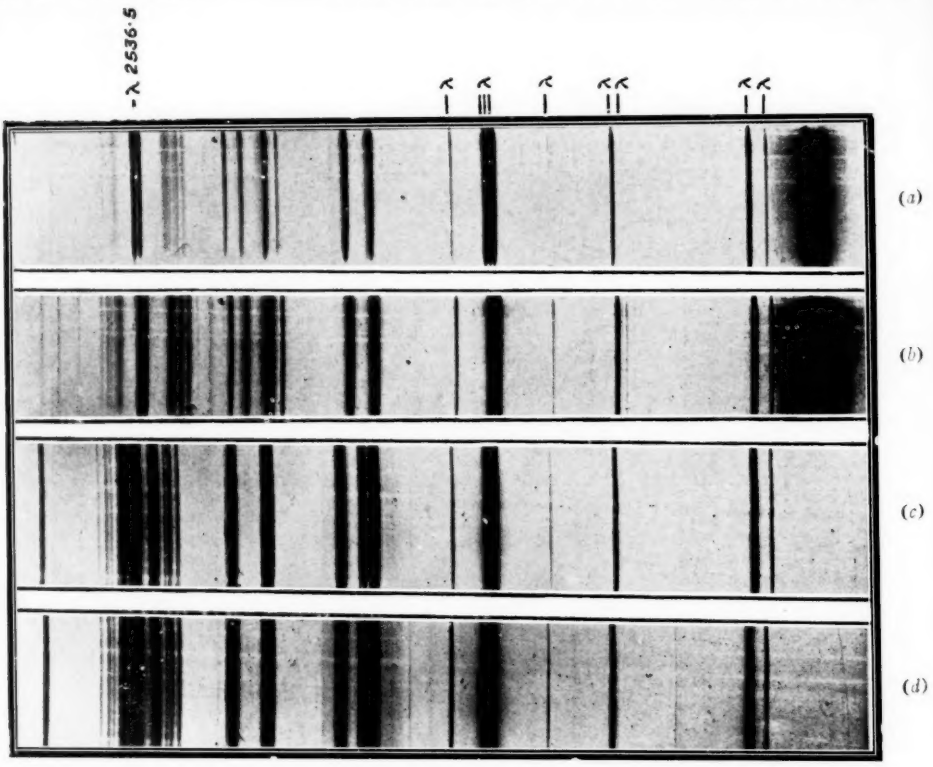


FIG. 10. (*a*) and (*b*) Gypsum, (*c*) and (*d*) Barytes, with two different exposures in each case

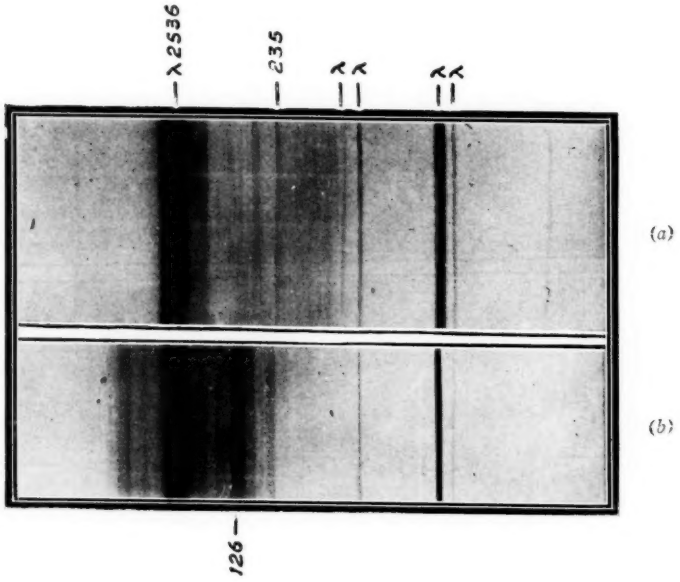


FIG. 11. (*a*) Rock-salt; (*b*) Potassium Bromide

The localisation of the internal vibrations permits of these overtones and summations appearing as frequency shifts with observable intensity. On the other hand, the continuous spectrum of elastic vibrations is completely inactive in light-scattering, apart from the particular case of a coherent reflection of the light waves by the elastic wave pattern.

References

1. Raman, C. V. .. *Molecular Diffraction of Light.*, 1922, Chap. VI. (Calcutta University Press.)
2. ———— .. *Ind. Jour. Phys.*, 1928, **2**, 387.
3. ———— .. *Proc. Ind. Acad. Sci.*, 1943, **18**, 237.
4. Narayanan, P. S. .. *Ibid.*, 1951, **34**, 1.
5. Krishnamurti, D. .. *Ibid.*, 1951, **33**, 325.
6. ———— .. *Ibid.*, 1951, **34**, this issue.
7. Krishnan, R. S. .. *Ibid.*, 1945, **22**, 329.
8. ———— .. *Ibid.*, 1945, **22**, 182.
9. ———— .. *Ibid.*, 1950, **31**, 435.
10. ———— .. *Ibid.*, 1946, **23**, 288.
11. ———— .. *Ibid.*, 1945, **22**, 274.
12. ———— .. *Ibid.*, 1947, **26**, 419.

THERMAL EXPANSION OF CRYSTALS

Part VIII. Galena and Pyrite

BY S. S. SHARMA

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received June 19, 1951

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. INTRODUCTION

THE results of interferometric studies on the thermal expansion of a number of cubic crystals were reported in these *Proceedings* (Sharma, 1950). The results of two more crystals, galena and pyrite, are set forth in the present paper. Both these crystals have been shown to exhibit some very interesting properties. According to Hearmon (1946) "the elastic constants measured on galena by Bhagavantam and Bhimasenachar (1944) yield a negative principal Young's modulus which is impossible. It would seem that the results for galena are due to some peculiarity of the material rather than the method." On the other hand, pyrite gives a positive Poisson's ratio. In view of these anomalous elastic properties it was thought worth while to study their thermal behaviour.

The only previous determination of the coefficient of linear expansion of galena is due to Fizeau (1868) at 40° C. Pyrite has been studied in the low temperature region up to about — 175° C. by Valentiner and Wallot (1915). Above the room temperature it has been studied by Press (1949) by employing crystal quartz interferometer plates. In the present investigation on pyrite not only have the measurements been extended to higher temperature, but the results obtained are different from the previous values.

2. RESULTS

The coefficients of linear expansion for galena and pyrite are set forth in Tables I and II respectively. The values calculated from the interpolation formula, set forth at the top of each table, are also inserted and the difference, in per cent., between these two sets of values is entered in the last column of each table.

The variation of α with temperature is represented graphically in Figs. 1 and 2 respectively.

TABLE I

Coefficient of linear expansion of galena at different temperatures

$\alpha_t = 0{\cdot}0_4 1843 + 0{\cdot}0_8 5071\ t + 0{\cdot}0_{10} 1176\ t^2$

Temperature	$\alpha \times 10^6$ (Observed)	$\alpha \times 10^6$ (Calculated)	Difference (%)
45·3	18·73	18·73	..
77·2	18·84	18·97	−0·7
108·6	19·10	19·23	−0·7
139·2	19·58	19·50	+0·4
169·1	19·91	19·80	+0·6
202·2	20·13	20·14	..
238·2	20·59	20·54	+0·2
273·5	20·95	20·97	..
308·0	21·35	21·42	−0·3
341·7	21·97	21·88	+0·4
374·6	22·36	22·36	..

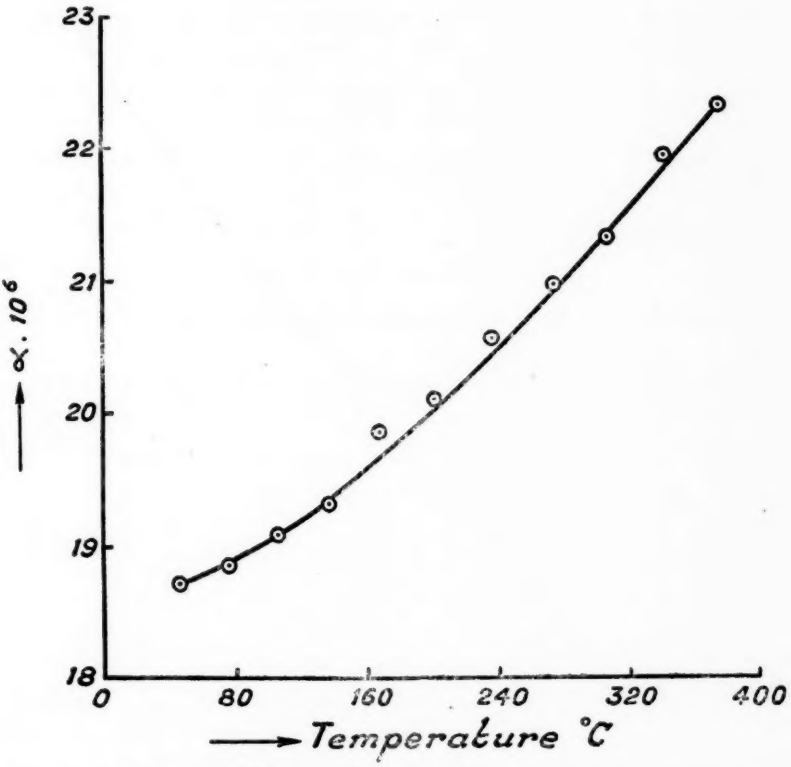


FIG. 1. Variation of coefficient of linear expansion for galena with temperature

TABLE II. *Coefficient of linear expansion for pyrite at different temperatures*

$\alpha_t = 0{\cdot}0_5 8401 + 0{\cdot}0_7 1125\, t + 0{\cdot}0_{11} 9168\, t^2$

Temperature	$\alpha \times 10^6$ (Observed)	$\alpha \times 10^6$ (Calculated)	Difference %
45·6	8·86	8·93	−0·8
76·5	9·26	9·32	−0·6
105·6	9·69	9·69	..
133·3	10·10	10·06	+0·4
159·6	10·50	10·43	+0·7
184·8	10·82	10·79	+0·3
213·2	11·17	11·22	−0·5
244·3	11·68	11·70	..
274·0	12·19	12·17	..
302·4	12·74	12·64	+0·8
329·6	13·13	13·11	..
349·5	13·52	13·45	+0·5

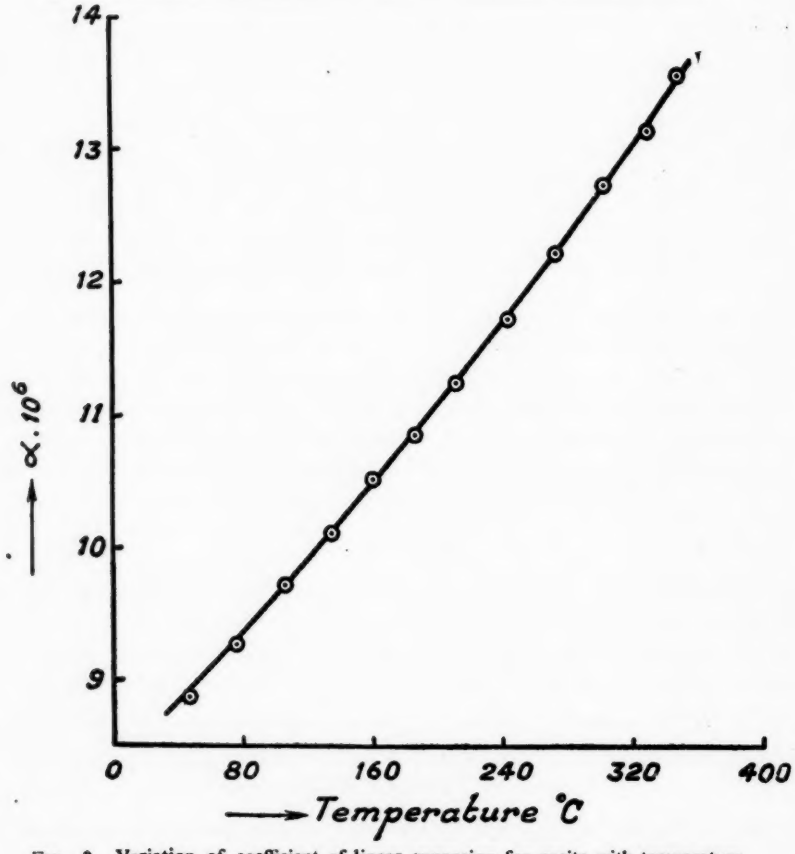


FIG. 2. Variation of coefficient of linear expansion for pyrite with temperature

The values for the coefficients of expansion for these two crystals available in the literature are entered in Table III and the author's values are also inserted for comparison.

TABLE III. *Comparative values for* α ($\times 10^6$) *for galena and pyrite*

Substance	Temperature (°C.)	Values in the literature	Values of the author	Authors
PbS ..	40	20·14	18·69	Fizeau (1868)
FeS_2 ..	40	9·07	8·87	Fizeau (1868)
	50	9·86	8·99	
	100	10·12	9·62	
	150	10·55	10·30	Press (1949)
	200	10·80	11·02	
	250	11·45	11·79	

It is obvious from this table that although author's values compare fairly well with those of Press after 150° C., the discrepancy between the two is considerable at lower temperatures. A similar difference was also noticed in the case of fluorite crystal (Sharma, 1950).

3. Evaluation of Grüneisen's Constant

Galena.—The calculated values of γ, the Grüneisen's constant, are entered in the last column of Table IV. For this purpose the molar specific heats at constant pressure, C_p, have been calculated from equation (1) given by Kelley

$$C_p = 10{\cdot}63 + 4{\cdot}01 \times 10^{-3}\,T. \qquad (1)$$

The value of compressibility has been taken from Bridgman's paper (1925).

TABLE IV. *Grüneisen's constant for galena at different temperatures*

Temperature (°C.)	C_p (Cals. deg.$^{-1}$ mol.$^{-1}$)	C_v (Cals. deg.$^{-1}$ mol.$^{-1}$)	$\alpha \times 10^6$ (deg.$^{-1}$)	γ
50	11·93	11·52	18·75	1·98
100	12·13	11·64	19·14	2·00
150	12·33	11·75	19·59	2·03
200	12·53	11·86	20·10	2·06
250	12·73	11·97	20·67	2·10
300	12·93	12·07	21·30	2·15
350	13·13	12·16	21·99	2·20
400	13·33	12·25	22·73	2·26

Pyrite.—For this crystal, the C_p values have been calculated from equation (2) taken from Kelley's paper (1934).

$$C_p = 10{\cdot}70 + 13{\cdot}36 \times 10^{-3}\,T. \qquad (2)$$

The value of compressibility has been taken from Bridgman's paper (1925).

TABLE V. *Grüneisen's constant for pyrite at different temperatures*

Temperature (°C.)	C_p (Cals. deg.$^{-1}$mol.$^{-1}$)	C_v (Cals. deg.$^{-1}$ mol.$^{-1}$)	$\alpha \times 10^6$ (deg.$^{-1}$)	γ
−165·0	5·25	5·24	2·95	1·37
−118·0	9·02	8·99	5·16	1·40
− 3·5	14·00	13·86	8·43	1·48
+ 50	15·02	14·83	8·99	1·50
100	15·68	15·44	9·62	1·55
150	16·35	16·05	10·30	1·59
200	17·02	16·66	11·02	1·64
250	17·69	17·26	11·79	1·70
300	18·36	17·85	12·60	1·75
350	19·02	18·43	13·46	1·81

In this table values at low temperatures have also been included. For this purpose the values of the coefficients of expansion have been taken from Valentiner and Wallot (1915) and those of thermal capacity from Eucken and Schwers (1913) as reported in Landolt and Bornstein's Tables (1931).

It will be seen from these values that γ values instead of remaining constant vary with temperature.

The author thanks Professor R. S. Krishnan for his constant interest in the work.

SUMMARY

The results of study of thermal expansion for galena and pyrite in the range (0–400)° C. are reported. It is found that the coefficients of linear expansion are respectively given by the formulæ

$$\alpha_t = 0{\cdot}0_4 1843 + 0{\cdot}0_8 6071\, t + 0{\cdot}0_{10} 1176\, t^2$$

and $$\alpha_t = 0{\cdot}0_5 8401 + 0{\cdot}0_7 1125\, t + 0{\cdot}0_{11} 9168\, t^2$$

Grüneisen's constant has been evaluated and is found to vary with temperature.

REFERENCES

Bhagavantam and Bhimsenachar .. *Proc. Ind. Acad. Sci.*, 1944, **20**, 298.
Bridgman .. *Sill. Journ.*, 1925, **10**, 483.
Eucken and Schwers .. *Verh. der Deuts. Ges.*, 1913, **15**, 583.
Fizeau .. *Comp. rend.*, 1868, **66**, 1005, 1072.
Hearmon .. *Rev. Mod. Phy.*, 1946, **18**, 409.
Kelley .. *Bull. Bur. Mines*, U.S.A., No. 371, **1934**.
Landolt and Bornstein .. *Phys. Chem. Tabellen*, II Erganz, 1931, **1244**.
Press .. *Proc. Ind. Acad. Sci.*, 1949, **20**, 284.
Sharma .. *Ibid.*, 1950, **31**, 83, 261, 339; **32**, **268**.
Vallentiner and Wallot .. *Ann. der Physik*, 1915, **46**, 837.

γ-SUBSTITUTION IN RESORCINOL NUCLEUS

Part VIII. Pechmann Condensation and Gattermann Formylation of α-Resorcylic Ester

BY C. S. MODY AND R. C. SHAH, F.A.SC.

(From the Organic Chemistry Laboratories, The Institute of Science, Bombay)

Received January 3, 1951

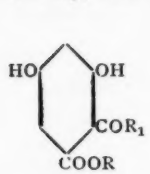
ORDINARILY, resorcinol and its derivatives are known to react in the β-position. Orcinol which is 5-methyl-resorcinol, however, manifests a marked tendency for substitution in the γ-position.[1] Thus, while β-substitution occurs on bromination,[2] Gattermann reaction[3] or Pechmann condensation with malic acid[4]; on carboxylation,[5] condensation with acetic acid,[5] or Pechmann condensation with ethyl acetoacetate[7], substitution takes place in the γ-position. Both β- and γ-positions simultaneously react on nitration,[8] nitrosation,[9] Reimer-Tiemann formylation[10] or Friedel-Crafts acylation.[11] As no satisfactory explanation has yet been put forward for this behaviour of orcinol, it was thought interesting to study the influence of a negative substituent, namely, carbmethoxy instead of methyl in the 5-position of the resorcinol nucleus, and hence some substitution reactions were carried out on methyl α-resorcylate.

Few instances of substitution of α-resorcylic acid derivatives are known. On bromination of the acid, the substitution takes place in the γ-position.[12] Nitration of its dimethyl ether also furnishes γ-substituted product.[13] The constitution of mono-substituted product obtained on nitration or chlorination of α-resorcylic acid has not been established.[14]

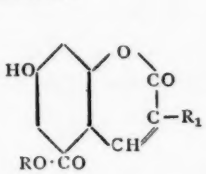
In the present work, Gattermann reaction and Pechmann condensation on methyl α-resorcylate has been studied.

Methyl α-resorcylate on Gattermann formylation gave methyl 3:5-dihydroxy-2-formylbenzoate (I, R = Me, R_1 ± H). The constitution has been assigned as an hydrolysis to the acid (I, R = R_1 = H) and subsequent decarboxylation, it gave β-resorcylaldehyde. On Knoevenagel condensation with ethyl acetoacetate and ethyl malonate, it (I, R = Me, R_1 = H) gave methyl 7-hydroxy-3-acetylcoumarin-5-carboxylate (II, R = Me, R_1 = COMe) and methyl 7-hydroxy-3-carbethoxycoumarin-5-carboxylate (II, R = Me, R_1 = COOEt) respectively. When dry hydrogen chloride was bubbled in the solution of the aldehyde (I, R = Me, R_1 = H) in ethyl acetate and acetophenone, the pyrylium salt, 7-hydroxy-5-carbmethoxyflavylium

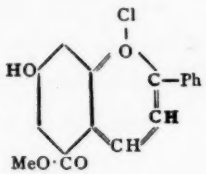
chloride (III) was obtained. When 3:5-dihydroxy-2-formylbenzoic acid (I, $R = R_1 = H$) was heated at about 250° for an hour a deeply coloured substance, probably 1:3:5:7-tetrahydroxy-4:8-diformyl-anthraquinone (IV, $R = H$), was obtained.



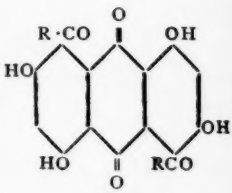
(I)



(II)

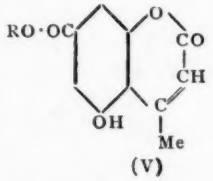


(III)

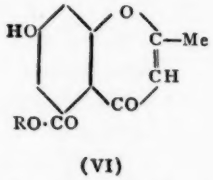


(IV)

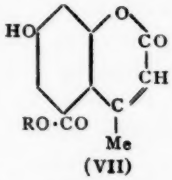
Methyl α-resorcylate on Pechmann condensation with ethyl acetoacetate in presence of concentrated sulphuric acid gave a mixture of products: an acid (A), m.p. 276–78° and two other products, (B), m.p. 249–50° and (C), m.p. 244–45°. The product B gave yellow coloration in alkaline solution and on hydrolysis furnished an acid (D), m.p. above 280°, which decarboxylated to give 5-hydroxy-4-methylcoumarin. Hence the product B was methyl 5-hydroxy-4-methylcoumarin-7-carboxylate (V, $R = Me$) and the acid D, 5-hydroxy-4-methylcoumarin-7-carboxylic acid (V, $R = H$). The product C on hydrolysis gave the acid A, which was also isolated from the reaction mixture. The acid A on decarboxylation gave 7-hydroxy-2-methylchromone and was therefore 7-hydroxy-2-methylchromone-5-carboxylic acid (VI, $R = H$) and the product C, its methyl ester (VI, $R = Me$). On keeping with sodium hydroxide solution (10%) for 48 hours, the chromone acid (VI, $R = H$) gave 3:5-dihydroxy-2-acetylbenzoic acid (I, $R = H$, $R_1 = Me$). It is interesting to note that attempts to prepare this compound by Friedel-Crafts acetylation of methyl α-resorcylate (V, *infra*) met with failures, and this seems to be the only method for its preparation. This acid (I, $R = H$, $R_1 = Me$) on heating at 210° for an hour gave a deep brown substance, probably 1:3:5:7 tetrahydroxy-4:8-diacetylanthraquinone (IV, $R = Me$).



(V)



(VI)



(VII)

α-Resorcylic acid on similar condensation with ethyl acetoacetate in presence of concentrated sulphuric acid gave only 7-hydroxy-2-methylchromone-5-carboxylic acid (VI, $R = H$).

The formation of chromone derivative, in presence of concentrated sulphuric acid, is of great interest, it being the third such observation. Dey and Lashminarayan[15] when they condensed β-naphthol with acetoacetic ester in presence of concentrated sulphuric acid, obtained a mixture of chromone and coumarin derivatives. Adams and Mercorney[16] also observed that 4-chloro-3 : 5-dimethylphenol on condensation with ethyl acetoacetate in presence of concentrated sulphuric acid gave a chromone derivative.

When methyl α-resorcylate was condensed with malic acid in presence of concentrated sulphuric acid, 7-hydroxycoumarin-5-carboxylic acid (II, $R = R_1 = H$) was obtained along with traces of its ester (II, $R = Me$, $R_1 = H$). The constitution was established as the acid (II, $R = R_1 = H$) on decarboxylation gave 7-hydroxycoumarin.

Methyl α-resorcylate failed to undergo Friedel-Crafts acylation with acetic anhydride or benzoyl chloride in presence of anhydrous aluminium chloride. Attempts to carry out Fries transformation of the diacetate or the dibenzoate were also unsuccessful.

The behaviour of α-resorcylic ester, is analogous to orcinol, the tendency for γ-substitution being greater in the former. The observed abnormal tendency for γ-substitution in the 5-substituted resorcinol derivatives does not appear to be due to any electromeric effect of the substituent, but may be attributed to its steric effect on the β-position.

On the same basis, can be explained, the formation of a 7-hydroxychromone along with a 5-hydroxy-4-methylcoumarin in the Pechmann condensation with ethyl acetoacetate, while a 7-hydroxycoumarin is formed in the condensation with malic acid. The carbmethoxy group does not exert any steric effect on the introduction of a CO or CH group in the β-position and a 7-hydroxychromone or a 7-hydroxycoumarin derivative is formed. However, the steric effect of the carbmethoxy in 5-position, on the introduction of $C\text{–}CH_3$ in 4-position required for the formation of a 7-hydroxy-4-methyl-5-carbmethoxycoumarin (VII), inhibits reaction in the β-position.

According to the mechanism as suggested by Robertson and coworkers[17], the enolic hydroxyl of the β-ketonic ester reacts either with the nuclear or phenolic hydrogen resulting in the formation of a coumarin or a chromone. The formation of a chromone along with a coumarin in the present case may be attributed to the deactivation of the molecule by the carbmethoxy group as a result of which both the nuclear hydrogen (in γ-position) as well as the phenolic hydrogen simultaneously react giving on cyclisation the two products. The failure of the Fries and Fridel-Crafts reactions may also

be attributed to the steric effect on the β-position and general deactivation of the molecule by the carbmethoxy group.

Experimental

Gattermann Reaction on Methyl α-Resorcylate: Methyl 3:5-*Dihydroxy-2-formylbenzoate* (*I*, $R = Me$, $R_1 = H$)

To a solution of methyl α-resorcylate (20 g.) in dry ether (200 c.c.) in a flask fitted with a mercury seal and a mechanical stirrer and cooled by freezing mixture, zinc cyanide (30 g.) was added. A stream of dry hydrogen chloride was then passed for 3 hours through the cooled stirred mixture. At the end a brown pasty mass was formed. The ether was decanted off and the aldimine hydrochloride obtained was hydrolysed by boiling with water (200–300 c.c.) for about 30 minutes. It was filtered and crystallised from hot water when *methyl* 3:5-*dihydroxy-2-formylbenzoate* (*I*, $R = Me$, $R_1 = H$) separated in long shining needles, m.p. 159-161° (12·4 g.) (Found: C, 55·5; H, 4·3. $C_9H_8O_5$ requires C, 55·1; H, 4·1%). It is soluble in hot water, readily soluble in methanol, ethanol and acetic acid. It gives deep red coloration with alcoholic ferric chloride. 2:4-*Dinitrophenylhydrazone*, separated in orange shining needles from acetic acid, m.p. 282–84° (decomp.) (Found: N, 15·3. $C_{15}H_{12}O_8N_4$ requires N, 14·9%). *Dimethyl ether*, obtained in long shining needles from rectified spirit, m.p. 107–08° (Found: C, 59·4; H, 5·4. $C_{11}H_{12}O_5$ requires C, 58·9; H, 5·3%).

The Gattermann reaction was also carried out by Shah and Laiwala's modified method,[18] using anhydrous aluminium chloride in dry ether; the same product, namely, methyl 3:5-dihydroxy-2-formylbenzoate was obtained.

Hydrolysis of Methyl 3:5-*Dihydroxy-2-formylbenzoate:* 3:5-*Dihydroxy-2-formylbenzoic Acid* (*I*, $R = R_1 = H$)

The above ester (I, R = Me, $R_1 = H$) (1 g.) was kept with sodium hydroxide solution (N, 16 c.c.) for 45 hours. It was acidified and extracted with ether. 3:5-*Dihydroxy-2-formylbenzoic acid* (*I*, $R = R_1 = H$) which was obtained on removal of ether was crystallised from hot water, pale brown needles, m.p. 230° (efferv.) (0·5 g.) (Found: C, 52·5; H, 3·1. $C_8H_6O_5$ requires C, 52·7; H, 3·3%).

Decarboxylation of 3:5-*Dihydroxy-2-formylbenzoic Acid* (*I*, $R = R_1 = H$): *β-Resorcylaldehyde*

The acid (I, $R = R_1 = H$) (0·5 g.) was dissolved in quinoline (5 c.c.), finely divided copper (0·5 g.) added and the mixture heated on an oil-bath at 200–05° for 20 minutes. The solution was filtered from the copper

powder, and dilute hydrochloric acid (2 N) added to it to remove quinoline. It was then extracted with ether, the ether extract washed with sodium bicarbonate solution, then with water and dried. On evaporation of ether β-resorcylaldehyde, m.p. and mixed m.p. 133–35°, was obtained. Tiemann and Leury[19] give m.p. 134–35°.

Knoevenagel Condensation of Methyl 3 : 5-*Dihydroxy-2-formylbenzoate* (*I*, $R = Me$, $R_1 = H$) *with Ethyl Acetoacetate : Methyl 7-hydroxy-3-acetylcoumarin-5-carboxylate* (*II*, $R = Me$, $R_1 = COMe$)

To a cooled mixture of ethyl acetoacetate (0·75 g.) and methyl 3 : 5-dihydroxy-2-formylbenzoate (0·5 g.), piperidine (6 drops) was added and the mixture was kept overnight. Next day the deep red solution was poured in very dilute hydrochloric acid. The yellow solid which separated was filtered and crystallised from rectified spirit in shining yellow needles, m.p. 224–25° (0·4 g.) (Found: C, 58·9; H, 4·5. $C_{13}H_{10}O_6$ requires C, 59·4; H, 4·1%). *Methyl 7-hydroxy-3-acetylcoumarin-5-carboxylate* (*II*, $R = Me$, $R_1 = COMe$) is insoluble in petroleum ether and benzene, but readily soluble in methyl and ethyl alcohols. It gives strong blue fluorescence in alkaline solutions.

Knoevenagel Condensation of Methyl 3 : 5-*Dihydroxy-2-formylbenzoate* (*I*, $R = Me$, $R_1 = H$) *with Ethyl Malonate : Methyl 7-hydroxy-3-carbethoxycoumarin-5-carboxylate* (*II*, $R = Me$, $R_1 = COOEt$)

Ethyl malonate (0·75 g.) was added to methyl 3 : 5-dihydroxy-2-formylbenzoate (0·5 g.) and the mixture cooled. Piperidine (6 drops) was then added and the mixture kept overnight. The yellow solid which separated on pouring in dilute hydrochloric acid on the next day, was filtered and crystallised from rectified spirit in thin yellow needles, (0·35 g.), m.p. 214–16° (Found: C, 57·4; H, 4·4. $C_{14}H_{12}O_7$ requires C, 57·4; H, 4·1%). *Methyl 7-hydroxy-3-carbethoxy-coumarin-5-carboxylate* (*II*, $R = Me$, $R_1 = COOEt$) was insoluble in benzene and petroleum, but readily dissolved in alcohols. It gave strong blue fluorescence in alkaline solutions.

7-Hydroxy-5-carbmethoxyflavylium Chloride (*III*)

To a cooled solution of methyl 3 : 5-dihydroxy-2-formylbenzoate (I, R = Me, $R_1 = H$) (0·5 g.) and acetophenone (0·5 g.) in dry ethyl acetate (5 c.c.), a slow stream of dry hydrogen chloride was passed. The solution gradually turned red and a crystalline product separated. After passing the gas for 4 hours, it was kept overnight. Next day the crystals were collected, washed with ethyl acetate and recrystallised from dilute hydrochloric acid, m.p. 216–18° (0·2 g.) (Found: C, 61·3; H, 4·4. $C_{17}H_{15}O_5Cl$

requires C, 60·9; 4·5%). *7-Hydroxy-5-carbmethoxyflavylium chloride* (*III*) gives red colouration with water and alkali and green fluorescence with concentrated sulphuric acid.

1 : 3 : 5 : 7-*Tetrahydroxy*-4 : 8-*diformylanthraquinone* (*IV*, $R = H$)

3 : 5-Dihydroxy-2-formylbenzoic acid (I, $R = R_1 = H$) was heated in an oil-bath at 250° for 1 hour, when 1 : 3 : 5 : 7-*tetrahydroxy*-4 : 8-*diformylanthraquinone* (*IV*, $R = H$) separated in red shining needles. It was boiled with little water to remove any unreacted original substance, and the crystals collected, m.p. above 280° (Found: C, 58·1; H, 2·6. $C_{16}H_8O_8$ requires C, 58·5; H, 2·4%). It is soluble in water and benzene and dissolves rapidly in alcohol. It gives deep red colouration with sodium hydroxide solution and orange coloration with concentrated sulphuric acid.

Pechmann Condensation of Methyl α-Resorcylate with Ethyl Acetoacetate: Methyl 5-Hydroxy-4-methylcoumarin-7-carboxylate (*V*, $R = Me$), *7-Hydroxy-2-methylchromone-5-carboxylic Acid* (*VI*, $R = H$) *and Methyl 7-Hydroxy-2-methylchromone-5-carboxylate* (*VI*, $R = Me$)

To a mixture of methyl α-resorcylate (20 g.) and ethyl acetoacetate (30 c.c.), concentrated sulphuric acid (90%; 120 c.c.) was added gradually with shaking and the mixture kept overnight. It was added to ice-cold water when yellow solid separated, which was filtered washed and dried (7·5 g.). The filtrate (A) was kept in a refrigerator. The solid was treated with sodium bicarbonate solution and immediately filtered off. The insoluble portion gave fluorescence in alkaline solution. It was thoroughly washed with water, dried and crystallised from rectified spirit, m.p. 203–10° (3·5 g.). It was repeatedly crystallised from rectified spirit till the product did not give fluorescence when pure *methyl 5-hydroxy-4-methylcoumarin-7-carboxylate* (*V*, $R = Me$) was obtained in faintly coloured needles, m.p. 249–50° (1·2 g.) (Found: C, 61·3; H, 4·3. $C_{12}H_{10}O_5$ requires C, 61·5; H, 4·3%). It is insoluble in water, benzene and chloroform and fairly readily soluble in alcohol. It dissolves in alkali giving deep yellow coloration. *Acetyl* derivative was crystallised from dilute alcohol in tiny needles, m.p. 168–69° (Found: C, 60·5; H, 4·1. $C_{14}H_{12}O_6$ requires C, 60·8; H, 4·3%).

The sodium bicarbonate solution from above was acidified when the free acid precipitated as a granular solid (2 g.). It was crystallised from rectified spirit in shining yellow needles, m.p. 276–78° (1·5 g.). It was found to be *7-Hydroxy-2-methyl chromone-5-carboxylic acid* (*VI*, $R = H$) (Found: C, 60·3; H, 3·3. $C_{11}H_8O_5$ requires C, 60·0; H, 3·6%). It gives faint blue fluorescence with alkali and concentrated sulphuric acid.

It is insoluble in chloroform and benzene and moderately soluble in alcohol and hot acetic acid.

From the filtrate (A) which was kept in a refrigerator some more of 7-hydroxy-2-methylchromone-5-carboxylic acid was obtained.

The filtrate from above was again kept in the refrigerator for 2–3 days, when another crystalline product separated. It was collected and crystallised from rectified spirit, m.p. 244–45° (1 g.) and was found to be *methyl 7-hydroxy-2-methylchromone-5-carboxylate* (*VI*, *R* = *Me*) (Found: C, 61·3; H, 4·1; $C_{12}H_{10}O_5$ requires C, 61·5; H, 4·3%). It is soluble in water and benzene and readily dissolves in methyl and ethyl alcohols. It gives faint blue fluorescence in alkaline solutions. *Acetyl* derivative was crystallised from dilute alcohol in colourless needles, m.p. 107–08° (Found: C, 60·7; H, 4·6. $C_{14}H_{12}O_6$ requires C, 60·8; H, 4·3%). *Benzoyl* derivative was crystallised from dilute alcohol in pale yellow needles, m.p. 139–40° (Found: C, 67·4; H, 4·2. $C_{19}H_{14}O_5$ requires C, 67·5; H, 4·1%).

Hydrolysis of Methyl 5-Hydroxy-4-methylcoumarin-7-carboxylate (*V*, *R* = *Me*): *5-Hydroxy-4-methylcoumarin-7-carboxylic Acid* (*V*, *R* = *H*)

The coumarin ester (V, R = Me) (1 g.) was hydrolysed by keeping in sodium hydroxide solution (40 c.c.; 10%) for 24 hours. *5-Hydroxy-4-methylcoumarin-7-carboxylic acid* (*V*, *R* = *H*), obtained on acidification of the above, was collected and crystallised from glacial acetic acid, long colourless needles, m.p. above 280° (0·5 g.) (Found: C, 60·3; H, 3·9. $C_{11}H_8O_5$ requires C, 60·0; H, 3·6%). It is easily soluble in methyl and ethyl alcohols and dissolved in alkali giving yellow solution.

Decarboxylation of 5-Hydroxy-4-methylcoumarin-7-carboxylic Acid (*V*, *R* = *H*): *5-Hydroxy-4-methylcoumarin*

The coumarin acid (V, R = H) (0·5 g.) was decarboxylated by heating in quinoline solution (7 c.c.) in presence of copper (1 g.) at 210–15° for 30 minutes. It was worked up as before when 5-hydroxy-4-methylcoumarin was obtained, crystallised from alcohol in needles, m.p. and mixed m.p. 263°. Sethna, Shah and Shah,[20] and Limaye and Kelkar[21] give the same m.p. Methyl ether, m.p. and mixed m.p. 140–42°. Limaye and Kelkar [21] give m.p. 143°.

Hydrolysis of Methyl 7-Hydroxy-2-methylchromone-5-carboxylate (*VI*, *R* = *Me*): *7-Hydroxy-2-methylchromone-5-carboxylic Acid* (*VI*, *R* = *H*)

The chromone ester (VI, R = Me) (1 g.) was kept with sodium hydroxide solution (1 N, 16 c.c.) for 48 hours, acidified, and 7-hydroxy-2-methyl-

chromone -5-carboxylic acid (VI, R = H) that separated was crystallised from rectified spirit, m.p. and mixed m.p. with the product already described, 276–78° (0·4 g.).

Decarboxylation of 7-Hydroxy-2-methylchromone-5-carboxylic Acid (VI, R = H): 7-Hydroxy-2-methylchromone

The chromone acid (VI, R = H) (0·5 g.) was dissolved in quinoline (7 c.c.), copper bronze added and heated at 160–70° for 30 minutes. It was worked up as usual and 7-hydroxy-2-methylchromone obtained was crystallised from rectified spirit, m.p. and mixed m.p. 250–51°. Kostanecki and Rozycki[22] give m.p. 249–50°. Methyl ether was crystallised from rectified spirit, m.p. and mixed m.p. 111–12°. Kostanecki and Rozycki[22] give m.p. 112°.

Hydrolysis of 7-Hydroxy-2-methylchromone-5-carboxylic Acid (VI, R = H): 3 : 5-Dihydroxy-2-acetylbenzoic Acid (I, R = H, R_1 = Me)

The chromone acid (VI, R = H) (1 g.) was kept with sodium hydroxide solution (10%; 40 c.c.) for 48 hours. It was then acidified and extracted with ether. The ether extract was dried, ether removed and 3 : 5-*dihydroxy 2-acetylbenzoic acid* (*I, R = H, R_1 = Me*) obtained was crystallised from hot water in shining yellow needles, m.p. 180° (efferv.) (0·4 g.) (Found: C, 50·2; H, 4·7. $C_9H_8O_5$ requires C, 50·5; H, 5·0%). It is soluble in hot water but insoluble in benzene and chloroform, readily soluble in methyl and ethyl alcohols. It gives violet coloration with alcoholic ferric chloride solution.

Decarboxylation of 3 : 5-Dihydroxy-2-acetylbenzoic Acid (I, R = H, R_1 = Me): Resacetophenone

3 : 5-Dihydroxy-2-acetylbenzoic acid (I, R = H, R_1 = Me) (0·2 g.) was decarboxylated in quinoline solution (3 c.c.) in presence of copper powder (0·2 g.), at 220–30° for 30 minutes. It was worked up as usual and resacetophenone obtained crystallised from water, m.p. and mixed m.p. 141–42°.

1 : 3 : 5 : 7-*Tetrahydroxy*-4 : 8-*diacetylanthraqyinone* (*IV, R = Me*)

3 : 5-Dihydroxy-2-acetylbenzoic acid (I, R = H, R_1 = Me) 0·2 g. was heated in an oil-bath at 210° for 1 hour. 1 : 3 : 5 : 7-*Tetrahydroxy*-4 : 8-*diacetylanthraquinone* (*IV, R = Me*) was obtained in deep brown needles, m.p. above 290° (Found: C, 59·9; H, 3·8. $C_{18}H_{12}O_8$ requires C, 60·6; H, 3·4%). It is readily soluble in alcohol. It gives deep purple colour with sodium hydroxide solution and reddish yellow colouration with concentrated sulphuric acid.

Pechmann Condensation of α-Resorcylic Acid with Ethyl Acetoacetate: 7-Hydroxy-2-methylchromone-5-carboxylic Acid (VI, R = H)

Concentrated sulphuric acid (25 c.c.) was added gradually with shaking to a mixture of α-resorcylic acid (5 g.) and ethyl acetoacetate (7·5 c.c.) and kept overnight. Next day the mixture was heated on a steam-bath for about 45 minutes, cooled and poured in ice-water. The yellow solid separated was collected and crystallised from rectified spirit, when 7-hydroxy-2-methylchromone-5-carboxylic acid separated, shining yellow needles, m.p. and mixed m.p. 276–78° (2·5 g.).

Pechmann Condensation of Methyl α-Resorcylate with Malic Acid: Methyl 7-Hydroxycoumarin-5-carboxylate (II, R = Me, R_1 = H) and 7-Hydroxycoumarin-5-carboxylic Acid (II, R = R_1 = H)

Concentrated sulphuric acid (20 c.c.) was added to a mixture of methyl α-resorcylate (5 g.) and malic acid (7·5 g.) and kept overnight. Next day it was heated on a water-bath for 1 hour, cooled and poured in ice-water. The solid separated was filtered, washed with water and finally with sodium bicarbonate solution. The residue was crystallised from rectified spirit, when *methyl* 7-hydroxycoumarin-5-*carboxylate* (*II*, R = *Me*, R_1 = *H*) separated in shining needles, m.p. 293–94° (Found: C, 59·4; H, 3·7. $C_{11}H_8O_5$ requires C, 60·0; H, 3·6%). It is moderately soluble in methyl and ethyl alcohols and gives strong blue fluorescence in alkaline solutions. *Acetyl* derivative was crystallised from dilute alcohol, m.p. 149–50° (Found: C, 59·4; H, 4·3. $C_{13}H_{10}O_6$ requires C, 59·5; H, 3·8%).

On acidification of sodium bicarbonate solution 7-*hydroxycoumarin-5-carboxylic acid* (*II*, R = R_1 = *H*) separated and was crystallised from dilute alcohol, shining needles, m.p. above 280° (1·5 g.) (Found: C, 58·6; H, 2·6. $C_{10}H_6O_5$ requires C, 58·2; H, 2·9%). *Acetyl* derivative was crystallised from dilute alcohol, tiny shining needles, m.p. 212–13° (Found: C, 58·6; H, 3·1. $C_{12}H_8O_6$ requires C, 58·1; H, 3·2%).

Hydrolysis of Methyl 7-Hydroxycoumarin-5-carboxylate (II, R = Me, R_1 = H): 7-Hydroxycoumarin-5-carboxylic Acid (II, R = R_1 = H)

The coumarin ester (II, R = Me, R_1 = H) (0·5 g.) was hydrolysed by keeping with sodium hydroxide solution (10%; 20 c.c.) for 48 hours. 7-Hydroxycoumarin-5-carboxylic acid (II, R = R_1 = H) obtained on acidification of the above solution was crystallised from dilute alcohol, thin shining needles, m.p. above 280°.

Decarboxylation of 7-hydroxycoumarin-5-carboxylic Acid (II, $R = R_1 = H$): 7-Hydroxycoumarin

The coumarin acid (II, $R = R_1 = H$) (0·5 g.) was dissolved in quinoline (7 c.c.) and copper powder (0·5 g.) added and heated at 200–10° for 30 minutes. On working up as usual 7-hydroxycoumarin, m.p. and mixed m.p. 223° was obtained. Pechmann[23] gives the same m.p. Methyl ether, crystallised from dilute alcohol, m.p. and mixed m.p. 110–12°. Pechmann[23] gives m.p. 112°.

Methyl 3: 5-Diacetoxybenzoate

Methyl α-resorcylate (10 g.) was refluxed with acetic anhydride (15 c.c.) and pyridine (10 drops) for 3 hours and poured in water. *Methyl 3: 5-diacetoxybenzoate* that separated was crystallised from a mixture of ether and petroleum, m.p. 58–59° (13·5 g.) (Found: C, 57·4; H, 4·6. $C_{12}H_{12}O_6$ requires C, 57·1; H, 4·8%).

Methyl 3: 5-Dibenzoyloxybenzoate

Methyl α-resorcylate (10 g.) was heated with benzoyl chloride (15 c.c.) and pyridine (10 drops) on a steam-bath for 2 hours. *Methyl 3: 5-benzoyloxybenzoate* that separated on pouring the above in water, was crystallised from methanol, tiny white needles, m.p. 79–80° (14 g.) (Found: C, 70·0; H, 4·2. $C_{16}H_{18}O_8$ requires C, 70·2; H, 4·3%).

Attempted Fries Transformations of Methyl 3: 5-Diacetoxybenzoate and Methyl 3: 5-Dibenzoyloxybenzoate

Attempts were made to carry out Fries transformation of the above esters using 1, 2 and 3 moles of anhydrous aluminium chloride at various temperatures and with nitrobenzene as solvent as well as without a solvent. However, no difinite product could be isolated.

Attempts to carry out Friedel-Crafts acylation on methyl α-resorcylate with acetic anhydride or benzoyl chloride, under various conditions of temperature and amount of aluminium chloride were also unsuccessful.

Summary

In continuation of the previous work[1] on substitution in derivative of orcinol, which is 5-methylresorcinol, substitution has been studied on methyl α-resorcylate; thus substituting the 5-methyl group of orcinol by a carbmethoxy group. On Gattermann formylation, methyl α-resorcylate furnished, as normally would be expected, methyl 3: 5-dihydroxy-2-formylbenzoate, substitution occurring in the β-position. On Pechmann condensation with ethyl acetoacetate in presence of concentrated sulphuric acid, it

gave three products: methyl 5-hydroxy-4-methylcoumarin-7-carboxylate, methyl 7-hydroxy-2-methylchromone-5-carboxylate and 7-hydroxy-2-methylchromone-5-carboxylic acid. The formation of a 7-hydroxy-chromone derivative, is interesting being the third observed instance of chromone formation during Pechmann condensation in presence of concentrated sulphuric acid. α-Resorcylic acid on Pechmann condensation with ethyl acetoacetate gave 7-hydroxychromone-5-carboxylic acid. On Pechmann condensation of methyl α-resorcylate with malic acid, the normal β-substitution occurred, giving 7-hydroxycoumarin-5-carboxylic acid along with its methyl ester. Thus, α-resorcylic ester, like orcinol, shows tendency for γ-substitution; and this tendency in 5-substituted resorcinol derivatives may be attributed to the steric effect rather than the electromeric effect of the substituent.

References

1. Saraiya and Shah .. *Proc. Ind. Acad. Sci.*, 1950, **31 A**, 213.
2. Fujikawa .. *Ber.*, 1935, **68 B**, 72.
3. Gattermann and Kobner .. *Ibid.*, 1899, **32**, 279.
4. Pechmann and Welsh .. *Ibid.*, 1884, **17**, 1469.
5. Bistrycki and Kostanecki .. *Ibid.*, 1885, **18**: 1986.
   Schwarz .. *Ibid.*, 1880, **13**, 1643
   Robertson and Robinson .. *J. Chem. Soc.*, 1927, 2199.
6. Raisinki .. *J. Prakt. Chem.*, 1882 (2), **26**, 59.
7. Pechmann and Cohen .. *Ber.*, 1884, **17**, 2188.
   Dey .. *J. Chem. Soc.*, 1915, **107**, 1614.
8. Meyer .. *Ber.*, 1903, **36**, 886.
   Nietzki and Mackler .. *Ibid.*, 1890, **23**, 720.
9. Henrich .. *Ibid.*, 1896, **29**, 989.
   ———— .. *Monatsh.*, 1897, **18**, 142.
10. Tiemann and Helkenbern .. *Ber.*, 1879, **12**, 1000.
11. Desai and Vakil .. *Proc. Ind. Acad. Sci.*, 1940, **12 A**, 398.
    —— and Schroff .. *J. Univ. Bombay*, 1941, **10** (3), 97.
12. Barth and Senhofer .. *Ann.*, 1872, **164**, 15.
13. Meyer .. *Monatsh.*, 1887, **8**, 430.
14. Zincke and Fuchs .. *Ber.*, 1892, **25**, 2687.
15. Dey and Laxshminarayan .. *J. Indian Chem. Soc.*, 1932, **9**, 153.
16. Adams and Mercorney .. *J. Amer. Chem. Soc.*, 1944, **66**, 802.
17. Robertson, Water and Jones *J. Chem. Soc.*, 1932, 1681.
18. Shah and Laiwala .. *Ibid.*, 1938, 1828.
19. Tiemann and Leury .. *Ber.*, 1877, **10**, 2212.
20. Sethna, Shah and Shah .. *J. Chem. Soc.*, 1939, 228.
21. Limaye and Kelkar .. *Rasayanam*, 1936, 45.
22. Kostanecki and Rozycki .. *Ber.*, 1901, **34**, 106.
23. Pechmann .. *Ibid.*, 1883, **16**, 2122.

γ-SUBSTITUTION IN RESORCINOL NUCLEUS

Part IX. Nuclear Benzylation of Some Polyhydroxy Ketones

By Bipin Z. Mullaji and R. C. Shah, F.A.Sc.

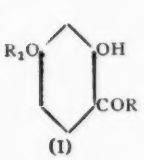
(*From the Organic Chemistry Laboratories, The Institute of Science, Bombay*)

Received January 3, 1951

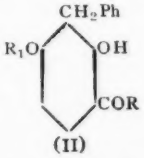
Herzig and Zeisel[1] observed that under the normal conditions of O-alkylation of phenols, certain polyhydroxy phenyl derivatives exhibit a tendency to undergo substitution in the benzene nucleus itself. Later Perkin[2] and almost simultaneously Gregor[3] as well as Weschler[4] independently observed that methylation of β-resorcylic acid with methyl iodide and potassium hydroxide gave 2-hydroxy-4-methoxy-3-methylbenzoic acid. Perkin[2], however, failed to similarly ethylate β-resorcylic acid, resacetophenone and β-resorcylaldehyde. Later Robinson and Shah,[5] basing their work on the observation of Crabtree and Robinson[6] that C-alkylation preceeds O-alkylation where excess of alkyl iodide and potassium hydroxide are used, were successful in nuclearly ethylating β-resorcylaldehyde, resacetophenone and methyl β-resorcylate. Shah and Shah[7] later extended this work to methylation of various 4-acylresorcinols.

In continuation of this work, nuclear benzylation has been studied with various acylresorcinols, namely, resacetophenone, respropiophenone, resbutyrophenone and resbenzophenone.

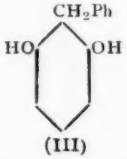
Resacetophenone (I, R = Me, R_1 = H) on benzylation with excess of benzyl chloride and potassium hydroxide gave 2-hydroxy-3-benzyl-4-benzyloxyacetophenone (II, R = Me, $R_1 = CH_2Ph$) along with 4-benzyloxy-2-hydroxyacetophenone (I, R = Me, $R_1 = CH_2Ph$). The former (II, R = Me, $R_1 = CH_2Ph$) on debenzylation gave 2 : 4-dihydroxy-3-benzylacetophenone (II, R = Me, R_1 = H), the constitution of which was proved by its synthesis by Hoesch reaction on 2-benzylresorcinol (III) with acetonitrile.



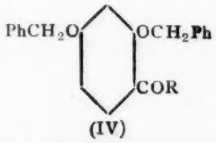
(I)



(II)



(III)



(IV)

Respropiophenone (I, R = Et, R_1 = H) and resbutyrophenone (I, R = Pr, R_1 = H) on similar treatment gave 2-hydroxy-3-benzyl-4-benzyloxy-

propiophenone (II, R = Et, $R_1 = CH_2Ph$) and 2-hydroxy-3-benzyl-4-benzyloxybutyrophenone (II, R = Pr, $R_1 = CH_2Ph$) respectively along with the corresponding 4-O-benzyl-respropiophenone and -resbutyrophenone (I, R = Et, $R_1 = CH_2Ph$ and I, R = Pr and $R_1 = CH_2Ph$ respectively). The former compounds (II, R = Et, $R_1 = CH_2Ph$ and R = Pr, $R_1 = CH_2Ph$) on debenzylation gave respectively 2:4-dihydroxy-3-benzylpropiophenone (II, R = Et, R_1 = H) and 2:4-dihydroxy-3-benzylbutyrophenone (II, R = Pr, R_1 = H). The constitutions were established by their synthesis by Hoesch reaction on 2-benzylresorcinol (III) with the corresponding nitriles.

Resbenzophenone (I, R = Ph, R_1 = H) gave a mixture from which the components could not be separated. Hence, the product was directly debenzylated when 2:4-dihydroxy-3-benzylbenzophenone (II, R = Ph, R_1 = H) and resbenzophenone were obtained. The constitution of the former (II, R = Ph, R_1 = H) was established by its synthesis by Hoesch reaction on 2-benzylresorcinol (III) with benzonitrile. 2:4-Dihydroxy-3-benzylbenzophenone (II, R = Ph, R_1 = H) on benzylation with benzyl chloride and potassium carbonate gave the corresponding 4-O-benzyl derivative (II, R = Ph, $R_1 = CH_2Ph$).

As the 2:4-dibenzyloxy derivatives of the above 4-acylresorcinols (IV) were expected to be formed during the course of this reaction they were also prepared by benzylation of the corresponding 4-O-benzyl derivatives (I, R_1 = Ph). Attempts to nuclearly benzylate 4-O-benzylresacetophenone (I, R = Me, $R_1 = CH_2Ph$) were unsuccessful, thus confirming the observation of Crabtree and Robinson.[6]

It is interesting to note that though the benzyl group has greater bulk than methyl or ethyl group, nuclear substitution is more facile in the case of benzyl than in the case of ethyl halide. This may be due to the fact that the halogen has enhanced reactivity when attached to the structure C: C. C. Cl found in allyl and benzyl chlorides.[8]

Experimental

Nuclear Benzylation of Resacetophenone : *2-Hydroxy-3-benzyl-4-benzyloxyacetophenone* (*II, R = Me, $R_1 = CH_2Ph$*)

Resacetophenone[5] (15·0 g.) was dissolved in methanolic potassium hydroxide (17·0 g., 3 mols. in 125 c.c.), benzyl chloride (38·0 g., 3 mols.) added and the mixture left overnight, when some solid separated. It was refluxed on a steam-bath for 5 hours, methanol was removed by distillation and excess of benzyl chloride by steam distillation. The residue, after

dilution with water, was extracted with ether, and the ether extract was washed several times with 10% alkali, then with water and dried. On removal of ether, an oily product was obtained which was extracted with hot alcohol. The alcohol extract on cooling deposited colourless needles of *2-hydroxy-3-benzyl-4-benzyloxyacetophenone* (*II*, $R = Me$, $R_1 = CH_2Ph$), m.p. 120–21° (3·4 g.) (Found: C, 79·1; H, 6·4. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·0%). It is insoluble in alkali and gives cherry-red coloration with alcoholic ferric chloride. It is soluble in acetic acid and chloroform and very soluble in benzene.

The oily residue that remained after treatment with hot alcohol, on distilling under reduced pressure, gave 2-hydroxy-4-benzyloxyacetophenone, m.p. and mixed m.p. 106–07°. Sheth, Gulati and Venkataraman[9] give m.p. 111°.

Debenzylation of 2-*Hydroxy-3-benzyl-4-benzyloxyacetophenone* (*II*, $R = Me$, $R_1 = CH_2Ph$): 2:4-*Dihydroxy-3-benzylacetophenone* (*II*, $R = Me$, $R_1 = H$)

A mixture of 2-hydroxy-3-benzyl-4-benzyloxyacetophenone (1·0 g.), glacial acetic acid (10 c.c.) and concentrated hydrochloric acid (5 c.c.) was refluxed for 2 hours. It was diluted and subjected to steam-distillation to remove benzyl alcohol and acetic acid. The residual liquid on cooling gave a solid which was crystallised from alcohol when 2:4-*dihydroxy-3-benzylacetophenone* (*II*, $R = Me$, $R_1 = H$) separated in colourless plates, m.p. 195–97° (0·5 g.) (Found: C, 73·9; H, 5·7. $C_{15}H_{14}O_3$ requires C, 74·4; H, 6·0%).

Hoesch Reaction on 2-*Benzylresorcinol* (*III*) *with Acetonitrile* : 2:4-*Dihydroxy-3-benzylacetophenone* (*II*, $R = Me$, $R_1 = H$)

Dry hydrogen chloride was passed through a mixture of ethereal solution (10 c.c.) of 2-benzylresorcinol (III, 1·5 g.), acetonitrile (0·5 g.) and fused zinc chloride (0·2 g.) for 3 hours at 0°. Ether was removed and the residue was diluted with water and boiled for 10 minutes. The product obtained on cooling was crystallised from dilute alcohol (charcoal) when colourless plates of 2:4-dihydroxy-3-benzylacetophenone (II, R = Me, $R_1 = H$) were obtained, m.p. and mixed m.p. 195–97° (0·2 g.).

Attempted Nuclear Benzylation of 2-*Hydroxy-4-benzyloxyacetophenone* (*I*, $R = Me$, $R_1 = CH_2Ph$)

2-Hydroxy-4-benzyloxyacetophenone (1·0 g.) was dissolved in a solution of potassium hydroxide (2·0 g.) in methyl alcohol (40 c.c.), benzyl chloride (4·0 g.) added, and kept overnight. The next day the mixture was

refluxed for 5 hours and methanol and benzyl chloride removed as in the previous case. On working up, 2-hydroxy-4-benzyloxyacetophenone m.p. and mixed m.p. 106–07° was recovered unchanged. No nuclearly benzylated product could be isolated.

Benzylation of 2-*Hydroxy*-4-*benzyloxyacetophenone* (*I*, $R = Me$, $R_1 = CH_2Ph$) 1 2 : 4-*Dibenzyloxyacetophenone* (*IV*, $R = Me$)

A mixture of 2-hydroxy-4-benzyloxyacetophenone (4·0 g.), benzyl chloride (8·0 g.) and anhydrous potassium carbonate (5·0 g.) in dry acetone (40 c.c.) was refluxed for 10 hours. Acetone was distilled off, and excess of benzyl chloride was removed by steam distillation. The residual solid was collected and washed several times with hot dilute alkali. The product that remained was washed with water and crystallised from rectified spirit when 2 : 4-*dibenzyloxyacetophenone* (*IV*, $R = Me$) separated in colourless needles, m.p. 81–82° (2·0 g.) (Found: C, 79·1; H, 5·5. $C_{22}H_{20}O_3$ requires C, 79·5; H, 6·0%).

Nuclear Benzylation of Respropiophenone : 2-*Hydroxy*-3-*benzyl*-4-*benzyloxypropiophenone* (*II*, $R = Et$, $R_1 = CH_2Ph$)

Respropiophenone[10] (3·0 g.) was dissolved in methanolic potassium hydroxide (3·2 g. in 25 c.c.), benzyl chloride (7·5 g.) was added and the mixture left overnight. The next day it was refluxed on steam-bath for 5 hours and methanol and benzyl chloride removed as in the previous case. The product was washed with sodium hydroxide (10%) and the residue crystallised from rectified spirit. After several crystallisations 2-*hydroxy*-3-*benzyl*-4-*benzyloxypropiophenone* (*II*, $R = Et$, $R_1 = CH_2Ph$), m.p. 120° (0·75 g.) was separated from the more soluble 2-*hydroxy*-4-*benzyloxypropiophenone* (*I*, $R = Et$, $R_1 = CH_2Ph$). 2-Hydroxy-3-benzyl-4-benzyloxy-propiophenone (II, R = Et, $R_1 = CH_2Ph$) is insoluble in alkali and gives cherry red coloration with alcoholic ferric chloride (Found: C, 80·3; H, 6·0. $C_{23}H_{22}O_3$ requires C, 79·8; H, 6·4%).

The mother liquor after the removal of the above gave 2-hydroxy-4-benzyloxypropiophenone, crystallised from rectified spirit, m.p. and mixed m.p. with an authentic specimen prepared as described below, 113–14° (Found: C, 75·5; H, 6·0; $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%).

Debenzylation of 2-*Hydroxy*-3-*benzyl*-4-*benzyloxypropiophenone* (*II*, $R = Et$, $R_1 = CH_2Ph$): 2 : 4-*Dihydroxy*-3-*benzylpropiophenone* (*II*, $R = Et$, $R_1 = H$).

A mixture of 2-hydroxy-3-benzyl-4-benzyloxypropiophenone (1 g.), glacial acetic acid (10 c.c.) and concentrated hydrochloric acid (5 c.c.) was

refluxed for 2 hours and worked up as in the previous corresponding experiment. The solid obtained was crystallised from rectified spirit when colourless plates of 2:4-*dihydroxy*-3-*benzylpropiophenone* (*II*, $R = Et$, $R_1 = H$) were obtained, m.p. 157–58° (0·2 g.) (Found: C, 74·6; H, 5·8. $C_{16}H_{16}O_3$ requires C, 75·0; H, 6·2%).

Hoesch Reaction on 2-*Benzylresorcinol* (*III*) *with Propionitrile :* 2:4-*Dihydroxy*-3-*benzylpropiophenone* (*II*, $R = Et$, $R_1 = H$)

Dry hydrogen chloride was passed through a mixture of 2-benzylresorcinol (1·0 g.) and propionitrile (0·55 g.) dissolved in ether (10 c.c.) and fused zinc chloride (0·22 g.) for 3 hours. It was then worked up as in the previous corresponding case. The product obtained on crystallisation from rectified spirit (charcoal) gave colourless plates of 2:4-dihydroxy-3-benzylpropiophenone, m.p. and mixed m.p. with the above product 157–58° (0·15 g.).

Benzylation of Respropiophenone : 2-*Hydroxy*-4-*benzyloxypropiophenone* (*I*, $R = Et$, $R_1 = CH_2Ph$)

A mixture of respropiophenone (2·5 g.), benzyl chloride (7·5 g.) and anhydrous potassium carbonate (2·1 g.) in dry acetone (15 c.c.) was refluxed for 8 hours. After removing acetone and benzyl chloride, the residue obtained was crystallised from rectified spirit which gave orange needles of 2-hydroxy-4-benzyloxypropiophenone, m.p. 113–14° (1·8 g.).

Benzylation of 2-*Hydroxy*-4-*benzyloxypropiophenone* (*I*, $R = Et$, $R_1 = CH_2Ph$) : 2:4-*Dibenzyloxypropiophenone* (*IV*, $R = Et$).

A mixture of 2-hydroxy-4-benzyloxypropiophenone (2·56 g.), benzyl chloride (7·0 g.) and anhydrous potassium carbonate (4·12 g.) in dry acetone (15 c.c.) was refluxed for 20 hours. Acetone and benzyl chloride were removed, the product was dissolved in hot rectified spirit. The first fraction of crystals of the unreacted monobenzyl ether, obtained on cooling was collected. The mother-liquor was concentrated and 2:4-*dibenzyloxypropiophenone* (*IV*, $R = Et$) obtained was crystallised from the same solvent, m.p. 64–65° (0·8 g.) (Found: C, 79·4; H, 5·7. $C_{23}H_{22}O_3$ requires C, 79·7; H, 6·1%).

Nuclear Benzylation of Resbutyrophenone : 2-*Hydroxy*-3-*benzyl*-4-*benzyloxy butyrophenone* (*II*, $R = Pr$, $R_1 = CH_2Ph$)

Resbutyrophenone[11] (9·0 g.) was dissolved in methanolic potassium hydroxide (8·9 g. in 100 c.c.), benzyl chloride (19·0 g.) was added and the mixture left overnight. The next day, it was refluxed for 5 hours, methanol

and benzyl chloride removed and the product washed with sodium hydroxide solution and worked up as described in the previous corresponding experiment. The residue obtained was fractionally crystallised from rectified spirit when 2-*hydroxy*-3-*benzyl*-4-*benzyloxybutyrophenone* (*II*, $R = Pr$, $R_1 = CH_2Ph$) was obtained in colourless needles, m.p. 108–09° (1·25 g.) (Found: C, 80·4; H, 6·7. $C_{24}H_{24}O_3$ requires C, 80·0; H, 6·7%). It was insoluble in alkali and gave cherry red coloration with alcohol ferric chloride.

From the filtrate 2-*hydroxy*-4-*benzyloxybutyrophenone* (*I*, $R = Pr$, $R_1 = CH_2Ph$) m.p. and mixed m.p. with an authentic specimen prepared as described below, 85°, was obtained (Found: C, 75·2; H, 6·4. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%).

Debenzylation of 2-*Hydroxy*-3-*benzyl*-4-*benzyloxybutyrophenone* (*II*, $R = Pr$, $R_1 = CH_2Ph$) : 2 : 4-*Dihydroxy*-3-*benzylbutyrophenone* (*II*, $R = Pr$, $R_1 = H$)

A mixture of 2-hydroxy-3-benzyl-4-benzyloxybutyrophenone (1·0 g.) glacial acetic acid (15 c.c.) and concentrated hydrochloric acid (7·5 c.c.) was refluxed for 3 hours. After working up as before, the product obtained was crystallised from rectified spirit, when colourless plates of 2 : 4-*dihydroxy*-3-*benzylbutyrophenone* (*II*, $R = Pr$, $R_1 = H$), m.p. 140–42° were obtained (Found: C, 76·0; H, 6·9. $C_{17}H_{18}O_3$ requires C, 75·5; H, 6·7%).

Hoesch Reaction on 2-*Benzylresorcinol* (*III*) *with Butyronitrile* : 2 : 4-*Dihydroxy*-3-*benzylbutyrophenone* (*II*, $R = Pr$, $R_1 = H$)

Dry hydrogen chloride was bubbled through a mixture of an ethereal solution (10 c.c.) of 2-benzylresorcinol (1·0 g.), butyronitrile (0·5 g.) and fused zinc chloride (0·23 g.) for 3 hours. It was worked up as in the previous case and the dark blue pasty product obtained was crystallised several times from rectified spirit (charcoal) when 2 : 4-dihydroxy-3-benzylbutyrophenone (II, R = Pr, R_1 = H) separated in colourless plates, m.p. and mixed m.p. 140–42° (0·15 g.).

Benzylation of Resbutyrophenone : 2-*Hydroxy*-4-*benzyloxybutyrophenone* (*I*, $R = Pr$, $R_1 = CH_2Ph$)

A mixture of resbutyrophenone (12·0 g.), benzyl chloride (33·4 g.) and anhydrous potasssium carbonate (18·4 g.) in dry acetone (50 c.c.) was refluxed for 8 hours. Acetone and benzyl chloride were removed. The product obtained was crystallised from rectified spirit, when 2-hydroxy-4-benzyloxy-butyrophenone (I, R = Pr, $R_1 = CH_2Ph$) separated in needles, m.p. 85° (9·0 g.).

Benzylation of 2-*Hydroxy*-4-*benzyloxybutyrophenone* (*I*, $R = Pr$, $R_1 = CH_2Ph$): 2:4-*Dibenzyloxybutyrophenone* (*IV*, $R = Pr$)

A mixture of 2-hydroxy-4-benzyloxybutyrophenone (9·0 g.), benzyl chloride (25·0 g.) and anhydrous potassium carbonate (15·8 g.) in dry acetone (50 c.c.) was refluxed for 20 hours. Acetone and benzyl chloride were removed as usual. The product was dissolved in hot rectified spirit. The first fraction of crystals of the unreacted monobenzyl ether, obtained on cooling, was removed. The mother-liquor on concentration gave crystals of 2:4-*dibenzyloxybutyrophenone* (*IV*, $R = Pr$), *m.p.* 61–62° (1·2 g.) (Found: C, 76·0; H, 7·0. $C_{24}H_{24}O_3$ requires C, 75·5; H, 6·7%).

Nuclear Benzylation of Resbenzophenone: 2:4-*Dihydroxy*-3-*benzylbenzophenone* (*II*, $R = Ph$, $R_1 = H$)

Resbenzophenone[12] (6·5 g.) was dissolved in methanolic potassium hydroxide (5·0 g. in 30 c.c.), benzyl chloride (11·4 g.) was added and the mixture kept overnight. The next day it was refluxed for 5 hours, methanol and benzyl chloride were removed and the product washed with sodium hydroxide solution. An oily product remained, which after several crystallisations gave a mixture, m.p. 69–94° (2·0 g.). As no pure product could be isolated from it, it (2·0 g.) was directly debenzylated by boiling with concentrated hydrochloric acid (10 c.c.) in acetic acid (20 c.c.) for 2 hours. On working up as usual, 2:4-*dihydroxy*-3-*benzylbenzophenone* (*II*, $R = Ph$, $R_1 = H$) was obtained, crystallised from rectified spirit in colourless plates, m.p. 159–60° (0·2 g.) (Found: C, 78·4; H, 5·3. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%).

On concentrating the filtrate after removal of the above product (II, R = Ph, R_1 = H), orange needles of resbenzophenone separated, m.p. and mixed m.p. 142–144°.

Hoesch Reaction on 2-*Benzylresorcinol* (*III*) *with Benzonitrile*: 2:4-*Dihydroxy*-3-*benzylbenzophenone* (*II*, $R = Ph$, $R_1 = H$)

Dry hydrogen chloride was passed through a mixture of 2-benzylresorcinol (1·0 g.), benzonitrile (0·5 g.) and fused zinc chloride (0·2 g.) in dry ether (10 c.c.) for 3 hours and subsequently worked up as usual. The dark blue solid residue was crystallised from rectified spirit (charcoal) when colourless needles of 2:4-dihydroxy-3-benzylbenzophenone, m.p. and mixed m.p. 159–60° (0·12 g.) separated.

Benzylation of 2:4-*Dihydroxy*-3-*benzylbenzophenone* (*II*, $R = Ph$, $R_1 = H$): 2-*Hydroxy*-3-*benzyl*-4-*benzyloxybenzophenone* (*II*, $R = Ph$, $R_1 = CH_2Ph$)

A mixture of 2:4-dihydroxy-3-benzylbenzophenone (0·2 g.), benzyl chloride (0·15 g.) and anhydrous potassium carbonate (0·13 g.) in dry acetone (10 c.c.) was refluxed for 8 hours. Benzyl chloride and acetone were removed. The residue after washing with sodium hydroxide was crystallised from rectified spirit when 2-*hydroxy*-3-*benzyl*-4-*benzyloxybenzophenone* (*II*, $R = Ph$, $R_1 = CH_2Ph$) separated in colourless needles, m.p. 92–93° (0·08 g.) (Found: C, 81·8; H, 5·2. $C_{27}H_{21}O_3$ requires C, 82·2; H, 5·6%).

Benzylation of Resbenzophenone: 2-*Hydroxy*-4-*benzyloxybenzophenone* (*I*, $R = Ph$, $R_1 = CH_2Ph$)

A mixture of resbenzophenone (6·5 g.), anhydrous potassium carbonate (8·28 g.) and benzyl chloride (15·8 g.) in dry acetone (30 c.c.) was refluxed for 8 hours. Acetone and benzyl chloride were removed. The product on crystallisation from rectified spirit gave orange needles of 2-*hydroxy*-4-*benzyloxybenzophenone* (*I*, $R = Ph$, $R_1 = CH_2Ph$), m.p. 120–21° (3·2 g.) (Found: C, 79·2; H, 5·2. $C_{20}H_{16}O_3$ requires C, 78·9; H, 5·3%).

Benzylation of 2-*Hydroxy*-4-*benzyloxybenzophenone* (*I*, $R = Ph$, $R_1 = CH_2Ph$): 2:4-*Dibenzyloxybenzophenone* (*IV*, $R = Ph$)

A mixture of 2-hydroxy-4-benzyloxybenzophenone (3·0 g.), benzyl chloride (5·0 g.) and potassium carbonate (2·7 g.) in dry acetone (15 c.c.) was refluxed for 10 hours. After removing acetone and benzyl chloride, the residue was washed several times with hot dilute sodium hydroxide solution. The insoluble portion, after washing with water, was crystallised from rectified spirit, when 2:4-*dibenzyloxy-benzophenone* (*IV*, $R = Ph$) was obtained, colourless plates, m.p. 116–17° (1·3 g.) (Found: C, 82·1; H, 5·8. $C_{27}H_{21}O_3$ requires C, 82·2; H, 5·6%).

Summary

In continuation of the work of Shah and collaborators[5, 7] on nuclear alkylation of resorcinol derivatives, nuclear benzylation has been studied with various 4-acylresorcinols, namely, resacetophenone, respropiophenone, resbutyrophenone and resbenzophenone. In all the cases the benzyl group was found to enter the γ-position giving 4-O-benzyl-3-benzylresacylophenones. The constitutions have been established by comparison of the debenzylated products, that is, 3-benzyl-resacylophenones, with the product obtained by Hoesch reaction on 2-benzylresorcinol with the corresponding acylnitrile.

Nuclear alkylation is found to be more facile with benzyl than with ethyl halide.

References

1. Herzig and Zeisel .. *Monatsh*, 1888, **9**, 217, 882 ; *et. seq.*
2. Perkin .. *J. Chem. Soc.*, 1895, **67**, 990.
3. Gregor .. *Monatsh*, 1894, **15**, 437.
4. Weschler .. *Ibid.*, 239.
5. Robinson and Shah .. *J. Chem. Soc.*, 1934, 1491.
6. Crabtree and Robinson .. *Ibid.*, 1918, **113**, 868.
7. Shah and Shah .. *J. Indian Chem. Soc.*, 1940, **17**, 32.
8. Conant, Kerner and Hussey .. *J. Amer. Chem. Soc.*, 1924, **46**, 232.
9. Sheth, Gulati and Venkataraman *J. Chem. Soc.*, 1934, 1765.
10. Pandit and Sethna .. *J. Indlan Chem. Soc.*, 1950, **27**, 1.
    Canter, Curd and Robertson .. *J. Chem. Soc.*, 1931, 1262.
11. Johnson and Lane .. *J. Amer. Chem. Soc.*, 1921, **43**, 348.
12. Shah and Mehta .. *J. Indian Chem. Soc.*, 1936, **13**, 368.
    Limaye and Munje .. *Rasayanam*, 1937, 80.

FARADAY EFFECT AND BIREFRINGENCE—II

Corundum

By S. Ramaseshan

(From the Department of Physics, Indian Institute of Science, Bangalore)

Received June 7, 1951

(Communicated by Prof. R. S. Krishnan, F.A.SC.)

1. Introduction

In most anisotropic crystals that have been studied so far [quartz; Disch (1903), Lowry (1912), cane sugar; Voigt (1908)] the Faraday rotation has been measured only along the optic axes. Chauvin (1890) has measured the rotation in a calcite crystal for directions of propagation two degrees away from the optic axis and he found practically no variation in the Faraday rotation. Becquerel and his collaborators (1928, 1929, 1930) have performed a series of elaborate experiments in some birefringent crystals which exhibit large paramagnetic rotations (tysonite, xenotime, etc.). They found the Faraday rotation to depend on the direction of propagation of light and were able to evaluate the Verdet constant parallel and perpendicular to the optic axis. A study of the literature revealed the absence of any magneto-optic data for corundum. This paper reports the values of the magneto-optic constants for this substance in the visible region when light travels along the optic axis. Measurements have also been made of the magnetic rotation for directions of propagation inclined to the optic axis with a view to find out whether the Verdet constant varies with direction. No such variation was found for inclinations upto 15° from the optic axis.

Corundum is pure Al_2O_3. It crystallises in the rhombohedral class of the hexagonal system with the fundamental rhombohedron differing very little in angle from a cube. The ratio of the length of the c-axis to that of a or b is 1·3630.

2. Magnetic Rotation along the Optic Axis

The specimens that were used for study were cut from synthetic boules of colourless corundum manufactured by the Verneuil process. This mode of production of single crystals involves the formation of irregular strains. A large number of thin plates were cut at various angles to the optic axis and were examined between crossed nicols with the light passing along the optic

axis. While the crystals were generally found to contain irregular strains, one specimen of thickness 1·180 mm. which showed very little residual strain was chosen for study. The optic axis of the specimen was inclined at an angle of 13° to the normal of the plate.

The crystal was mounted on a flat brass plate consisting of two concentric rings which could rotate with respect to each other. There was a central hole of 6 mm. diameter in the inner ring. The brass plate was supported vertically by a rod which could be rotated about the vertical axis by a graduated head which could be turned by a worm wheel. By this arrangement the crystal could be rotated through known angles about vertical and horizontal axes. The crystal was placed between the pole pieces of a Faraday effect magnet fixed to this apparatus. Parallel plane polarised monochromatic light (λ 5,461) with its electric vector vertical was made to pass through the crystal *exactly* along the optic axis and the rotation due to the magnetic field was measured with the aid of a half shade at the analyser end. The final rotation recorded for any magnetic field was a mean of about 100 readings. The effective magnetic field was determined by noting the magnetic rotation produced in a crown glass plate of thickness 1·29 mm. placed exactly in the position of the crystal plate. The Verdet constant of the glass plate had been accurately determined previously to $\frac{1}{3}\%$. The Verdet constant of the crystal was calculated using the Verdet Law.

$$\theta = \mathrm{VH}t \cos (i - r)/\cos r,$$

where θ is the rotation, H is the field, i and r are the angles of incidence and refraction and t is the thickness of the specimen. As was to be expected the Verdet constant was lower with other specimens that showed greater residual birefringence. Table I gives the measured data together with the

TABLE I

Magneto-optic constants in Alumina along the optic axis

Effective thickness = 1·190 mm.
Effective field = 15400 Oersteds.

λ in A.U.	Refractive Index		Rotation ρ in minutes	Verdet constant V per cm. per oersted	Magneto-optic anomaly γ (in per cent)
	μ_ω	μ_ϵ			
5893	1·7685	1·7605	38·5	0·0210	64·0
5461	1·7712	1·7630	44·0	0·0240′	65·6
4358	1·7823	1·7739	70·5	0·0386′	65·0

calculated values of the Verdet constant and magneto-optic anomaly, for the three wavelengths λ 5,893, λ 5,461 and λ 4,358.

3. Magnetic Rotation away from the Optic Axis

For measurements along directions inclined to the optic axis, the optic axis was first made to lie in the horizontal plane and the crystal was then rotated through known angles about the vertical axis by turning the worm wheel. It may be mentioned that the crystal could be accurately rotated through angles of the order of 20″ of arc. Since the incident light had its plane of vibration vertical, the emergent light which was also plane polarised could be extinguished by a perpendicular nicol. When the magnetic field is put on, the emergent light becomes elliptically polarised with its major axis rotated through an angle ψ with respect to the plane of vibration of the incident light. This angle ψ was measured with a half shade at the analyser end for different angles of incidence. In these measurements it is absolutely necessary to have the incident light accurately parallel, a divergence or convergence of a fifth of a degree being sufficient to vitiate the results.

If the plane of vibration of the incident light coincides with one of the principal planes of the solid, then ψ is given by the following two formulæ under appropriate conditions (Ramaseshan, 1951)

$$2\psi = 2\rho\,(1 - \delta^2/3!) \text{ when } \delta \text{ is small}$$

and $$\tan 2\psi = \frac{2\rho}{\Delta} \sin \Delta \text{ when } 2\rho/\delta \text{ is small,}$$

where ρ is the total magnetic rotation in the hypothetical case when birefringence is absent and δ and Δ are respectively the total phase retardations when rotation is absent and present. In the case of alumina the approximations $\tan 2\psi = 2\psi$ and $\Delta = \delta$ can be made when the direction of propagation makes an angle greater than 7° with the optic axis. The value of δ when the direction of propagation makes an angle ϕ with the optic axis is given by

$$\delta = \frac{2\pi}{\lambda} t\,(n_{\epsilon\phi} - n_\omega) = -\frac{2\pi}{\lambda} t \left[1 + 3/2 \frac{n_\omega - n_\epsilon}{n_\epsilon}\right] [n_\omega - n_\epsilon] \sin^2 \phi,$$

where t is the thickness. In the case of alumina for λ 5,461 $n_\omega - n_\phi = 0{\cdot}008257 \sin^2 \phi$. Using this and the two formulæ given above and assuming that the Verdet constant does not change with direction (*i.e.*, ρ in any direction has the same value as that along the optic axis) the values of ψ have been calculated.

The solid curve in Fig. 1 gives the theoretical variation of with ψ with ϕ. The crosses are the experimental points. These lie very nearly on the theoretical curve thus showing that the Verdet constant does not sensibly change

for inclinations up to 15° away from the optic axis. This is not surprising as the optical properties of corundum do not vary appreciably with direction, the birefringence being of the order of 0·01.

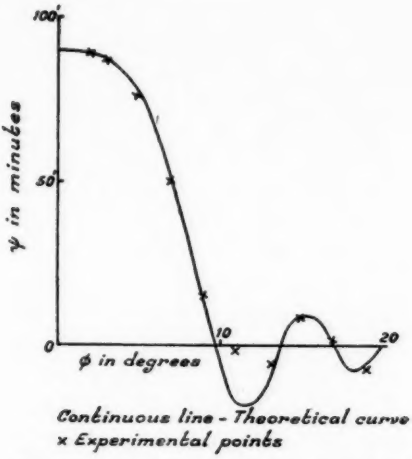


FIG. 1. Variation of ψ with ϕ in corundum

The author wishes to thank Professor R. S. Krishnan for the kind interest he took in this investigation and to Dr. G. N. Ramachandran for the helpful discussions he had with him.

SUMMARY

The Verdet constant and the magneto-optic anomaly for corundum for light travelling along the optic axis have been determined for the wavelengths λ 5,893, λ 5,461 and λ 4,358. The Verdet constant has the values $V_{5893} = 0{\cdot}0210'$, $V_{5461} = 0{\cdot}0240'$ and $V_{4358} = 0{\cdot}0381'$ minutes per cm. per Oersted and γ has a value of 0·64. Accurate measurements have also been made for directions of propagation inclined to the optic axis and it is found that the Verdet constant does not sensibly change for an inclination of about 15° away from the optic axis.

REFERENCES

Becquerel .. *Leiden Communications*, 188, 191, 193, etc. (1928, 1929, 1930).
Chauvin .. *Jour. de Physique*, 1890 (2), **9**, 5.
Disch .. *Ann. der Phys.*, 1903, **12**, 1153.
Lowry .. *Phil. Trans.*, 1912, **212 A**, 261.
Ramaseshan .. *Proc. Ind. Acad. Sci.*, 1951, **34 A**, 32.
Voigt .. *Phys. Z. S.*, 1908, **9**, 689.

ACCELERATED OXIDATION OF COTTON CELLULOSE IN PRESENCE OF REDUCING SUBSTANCES—PART III

By G. D. Joshi and G. M. Nabar, F.A.Sc.

(From the Department of Chemical Technology, University of Bombay)

Received October 9, 1950

Introduction

Mhatre, Nabar and Vyas[1] have investigated the accelerated oxidation of cellulose by hypochlorite solutions in presence of a number of reducing substances such as leuco compounds of vat dyes belonging to different chemical structure and also ferrous hydroxide and have arrived at the following conclusions:

(1) The rate of oxygen transfer, the amount of oxygen transferred and the pH for maximum oxygen uptake by the cellulose substrate depend on the particular reducing substance present on the fibre during the oxidation.

(2) With at least twelve leuco vat dyes examined in detail, there exists no similarity between the pH-corrected oxidation potential[2] curve and the curves showing relation between pH and oxygen uptake and pH and cuprammonium fluidity.

(3) At 30° C., the corrected oxidation potential as obtained by applying a correction of $0{\cdot}06 \times$ pH to the measured value of the potential, is not a measure of the oxidising intensity of hypochlorite solutions.

(4) Although for each of the dyes examined, the similarity in shape of curves relating pH to (*a*) oxygen consumed, (*b*) cuprammonium fluidity, (*c*) copper number and (*d*) carboxylic acid content does not materially alter, each accelerator is found to have a specific influence on the degree of oxidation. Further the oxidation accelerated by leuco compounds of vat dyes such as Cibanone Orange R, Cibanone Yellow R, Caledon Yellow GN, etc., shows a maximum intensity of oxidation at about pH 7·3. By replacing the accelerating system by leuco Ciba Blue 2 B or ferrous hydroxide, the pH for maximum oxidation is shifted to 6·3 while with leuco compounds of Caledon Jade Green XS, Caledon Green BS and Indanthren Dark Blue BO the pH for maximum oxidation is at about 5·4.

From the foregoing it is clear that the reducing substance present on cellulose maintains its identity as seen by the shift in the pH at which maximum chemical attack takes place and that it is some intrinsic physico-chemical property of the reducing substance present on cellulose during the oxidation that is responsible for this acceleration.

In an attempt to explain the accelerated oxidation of cotton cellulose by hypochlorite in presence of reduced Cibanone Orange R, Nabar, Scholefield and Turner[2] suggested that an estimate of the intensity of oxidation may be given either by (*a*) the difference between a value representing the measured potential of sodium hypochlorite solution and a value representing the oxidation-reduction potential of the cellulose substrate or (*b*) the difference between the measured oxidation potential of the hypochlorite solution and the oxidation-reduction potential of the reduced Cibanone Orange R present on the fibre. The first suggestion has been critically examined in the earlier communication of this series,[3] and it has been shown that it does not stand to experimental investigation. The present paper deals with an account of the investigation concerning the second suggestion made by the above authors.[2]

Electrical measurements on the system leuco vat dye $\leftrightharpoons$ vat dye are not easy to carry out owing to the extremely low solubility of these compounds in aqueous medium. This is further complicated by pH of the medium which directly influences the dissociation of the weakly acidic dissociable groups of the leuco compounds.

In the present investigation, experimental difficulties have been considerable and in spite of the accumulation of considerable data, it has not yet been possible to put forward a full theoretical explanation of the significance of the results. Nevertheless they give a clear indication of the part played by the reducing substances in bringing about an accelerated oxidation of cellulose by hypochlorite solutions.

Two dyes, Cibanone Orange R and Ciba Blue 2 B, were selected for the experimental investigation. These were dyed according to usual dyeing practice on loose cotton and yarn, previously purified. The redox potentials of the two vat dyes while upon the fibre were then measured by a new method developed after a considerable experimentation.[4, 5]

It is shown that there is a very close similarity between the curve showing the relationship of pH to the difference in the oxidation potential of the hypochlorite and the reduction potential of the leuco vat dye and the curve showing the relation between the pH of the oxidising medium and the

oxygen consumed by the leuco vat dyed cotton. This observation is further supported by the straight line relationship existing between the oxygen consumption and the difference in the oxidation potentials of the hypochlorite and the reduction potentials for both the dyes.

Experimental Methods

Cotton.—Cotton in the form of yarn and loose cotton was used. It was purified according to the method employed for the preparation of standard cellulose.[6]

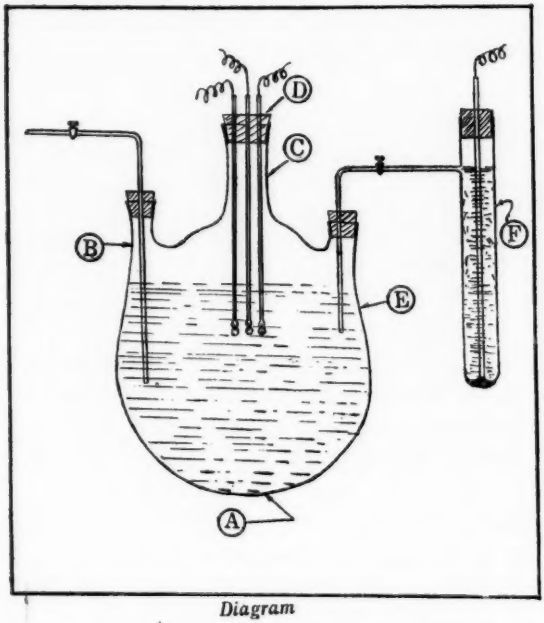
Method of dyeing.—Two per cent. dyeings of Cibanone Orange R and Ciba Blue 2 B were prepared. The dyestuff was carefully vatted and the dyeing was carried out at 60° C. in a dark room for ¾ of an hour. After the dyeing was complete the oxidation was allowed to take place slowly in cold running water. The full details of the method are given elsewhere.[2]

Reduction of the dyeing and the determination of oxygen consumption.—Ten grams of the dyed yarn was treated with 2% cold solution of sodium hydrosulphite, the leuco-vat dyed yarn thus obtained was washed thoroughly with oxygen free cold distilled water and then treated with a suitably buffered sodium hypochlorite solution. This was carried out strictly adhering to details described by Nabar, Scholefield and Turner.[2]

Determination of the reduction potential of vat dyes.—The method used is similar to the one used by Mhatre and Nabar[4] for the determination of the reduction potential of ferrous hydroxide. The electrode consists of a stout platinum wire sealed in a bulb blown at the end of a glass tube 3 mm. diameter. The electrodes were properly cleaned, adhering to details described by Mhatre and Nabar.[4]

Loose cotton dyed with the vat dyestuff was wrapped tightly round the platinum wire. Clean mercury was then filled in the glass tube. Three such electrodes were fixed in a rubber stopper and placed in boiling distilled water so as to remove all the occluded air from the dyed cotton. This also serves to bring about an initial wetting out of the cotton. The electrodes were then immersed in a 2% solution of sodium hydrosulphite to bring about the reduction of the vat dye. The reduced dyeings on the electrode were then immersed at once in cold air-free distilled water. The electrodes were moved backwards and forwards below the surface of water for one minute and then transferred to another such bath. This was repeated three times and then immediately immersed in a buffer solution which was boiled sufficiently and cooled to 30° C., while purified hydrogen was vigorously bubbled in,

The apparatus used is shown in the diagram.



Diagram

A is a three-necked flask in which the boiled out buffer solution is kept. Through the neck *B*, the hydrogen gas is bubbled in, while the buffer is being cooled. In the neck *C*, the stopper *D*, carrying the electrodes, is fixed. The neck *E* carries a saturated calomel half cell *F*. The end of the side tube of the electrode vessel was sealed by an agar agar jelly in order to prevent rapid diffusion of potassium chloride solution into the buffer. After the buffer had been cooled to nearly 30° C., the whole apparatus was kept in a thermostat adjusted to 30° C. $\pm$ 0·1. The bubbling of purified hydrogen gas was continued for about 15 minutes more in order to allow the buffer to attain a temperature of 30° C. $\pm$ 0·1. The bubbling was then stopped and the neck *B* was tightly stoppered with a rubber bung.

The two electrodes, *i.e.*, the platinum electrode and the calomel electrode *F* thus formed a cell and the potential of the cell was then measured using Cambridge Scientific Instrument Company's valve potentiometer. The measurements of E.M.F. were made at an interval of about 5 minutes, until a stable value was reached. For this, the experiment had to be continued for a period of over three hours. The readings were plotted against time

and the horizontal portion of the curve was taken to represent the potential of the leuco-vat dye at that pH value.

Three electrodes were used for each pH value and the average of these was taken. Sometimes an electrode behaved erratically and so was discarded. The value was accepted only when it was reproduced. For each pH value, the whole experiment was independently repeated twice or thrice using new platinum electrodes and it was found that the values were reproducible with good accuracy. The actual measurement consists in determining the e.m.f. of the following cell:—

$+Hg \;/\; Hg_2Cl_2$, sat. KCl // sat. KCl // Leuco-vat dyed cotton in buffer solution / Pt$^-$

$\longleftarrow$ 0·245 volts $\longrightarrow$ E volts

$\longleftarrow$ X_2 volts

$E = X_2 - 0{\cdot}245$, where E is the reduction potential.

Two typical curves for Ciba Blue 2 B showing the behaviour of the electrodes in acid pH and alkaline pH are shown in Figs. 1 and 2 respectively.

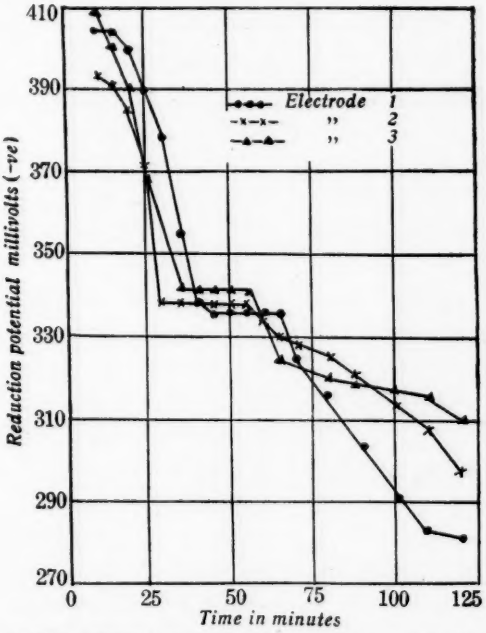


FIG. 1. Relation between lime of measurement and reduction potentials of Ciba Blue 2 B at pH 6·15

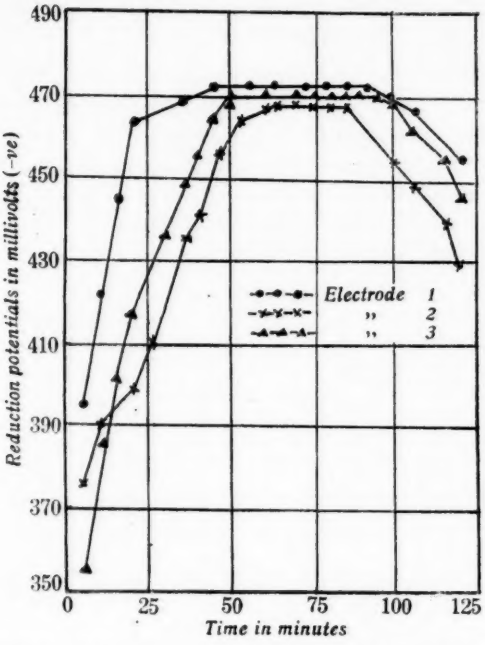


FIG. 2. Relation between time of measurement and the reduction potential of Ciba Blue 2 B at pH 8·36

It was found that on alkaline side, the values go on increasing with time, reach a stable value and then fall slowly; while on acid side the values fall continuously from the beginning, reach a stable value and then again fall rapidly.

It is found that the ease of measurement and the stability of the equilibrium on alkaline side is much greater than that on the acid side. To ensure that the potential developed when the leuco-vat dyed cotton is in contact with the platinum wire, is due to the presence of the leuco-vat dye only, blanks were carried out with the following systems:

(1) Hg^{+} / Hg_2Cl_2, Sat. KCl // Sat. KCl solution // air-free buffer solution / Pt⁻

(2) Hg^{+} / Hg_2Cl_2, Sat. KCl // Sat. KCl solution // loose dyed cotton in air-free buffer solution / Pt⁻

Experiments were done exactly under the same conditions as those when determining the reduction potential of the vat dye and it was found that in neither case, stable and reproducible potential could be established.

Calibration of the glass electrode.—The glass electrode is not reliable for the determination of pH values higher than 9·5 and was hence calibrated for pH values between 9 and 12 with buffers of known pH.

Experimental Results

The experimental results are described in Tables I to VI. The measured values of the reduction potentials for Cibanone Orange R and Ciba Blue 2 B are given in Tables I and II respectively and the relation between the reduction potentials and pH for the two dyes is graphically shown in Figs. 3 and 4 respectively.

Examination of these curves shows a resemblance to a neutralization curve of polybasic weak acid group by group. Further it is seen that the number of inflexions in the curve for any particular dye are definite. In the case of Cibanone Orange R, these are four, while in case of Ciba Blue 2 B these are only two.

Table I

Relation between pH and reduction potential of Cibanone Orange R

(Each value of redox potential is a mean of three independent measurements)

pH of the buffer solution	Measured potentials (millivolts)			Mean
	Expt. 1	Expt. 2	Expt. 3	
11·75	744·3	744·6	..	744·4
11·40	662·5	667·0	660·7	660·7
11·00	645·5	644·0	..	644·7
10·80	627·7	629·0	..	628·2
10·15	582·0	585·5	582·0	583·6
9·58	558·5	558·5	..	558·5
9·15	527·5	524·5	523·5	525·7
8·68	481·0	482·5	..	481·7
8·02	448·5	451·0	..	449·7
7·55	433·5	435·5	..	434·5
7·25	417·0	414·5	..	415·5
6·95	389·5	385·5	388·5	387·7
6·55	359·5	358·9	..	359·2
6·06	317·5	321·5	..	318·7
5·92	310·5	309·0	..	319·7
5·38	300·0	299·7	303·5	302·0
4·95	281·0	276·5	281·5	279·3

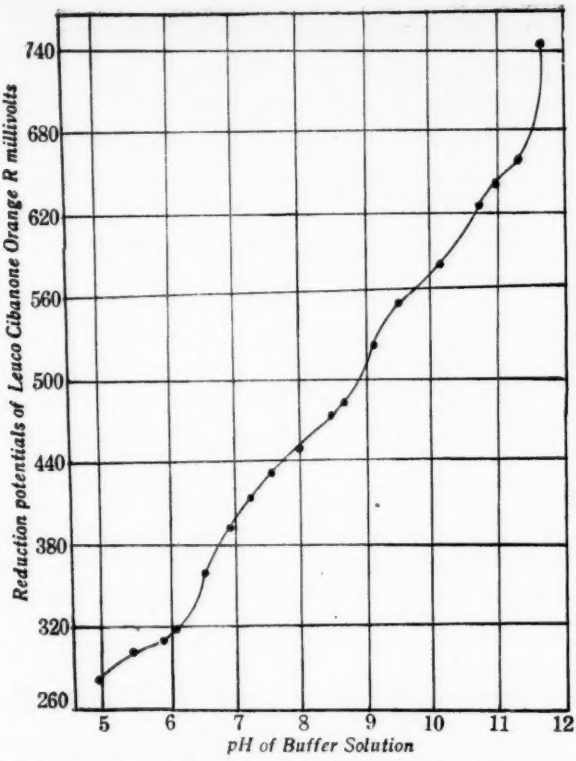


FIG. 3. Relation between pH and the reduction potential of Cibanone Orange *R*

TABLE II

Relation between pH and reduction potential of Ciba Blue 2 B

pH of the buffer solution	Measured potentials (millivolts)			Mean
	Ext. 1	Expt. 2	Expt. 3	
11·75	734·0	737·0	..	735·5
11·20	657·5	659·9	..	658·2
10·68	612·0	611·5	..	611·7
10·00	561·5	562·5	564·5	563·0
9·55	547·5	545·5	..	546·8
9·15	522·0	522·5	..	522·3
8·36	485·0	487·5	490·0	488·7
7·65	423·5	422·5	..	423·2
7·02	390·5	392·5	..	391·5
6·72	378·0	378·5	..	378·3
6·34	362·5	365·5	364·0	364·5
6·15	339·0	336·5	..	338·0
5·83	309·5	302·0	..	305·6
5·30	286·0	286·0	..	286·0
4·85	272·5	265·5	..	267·3

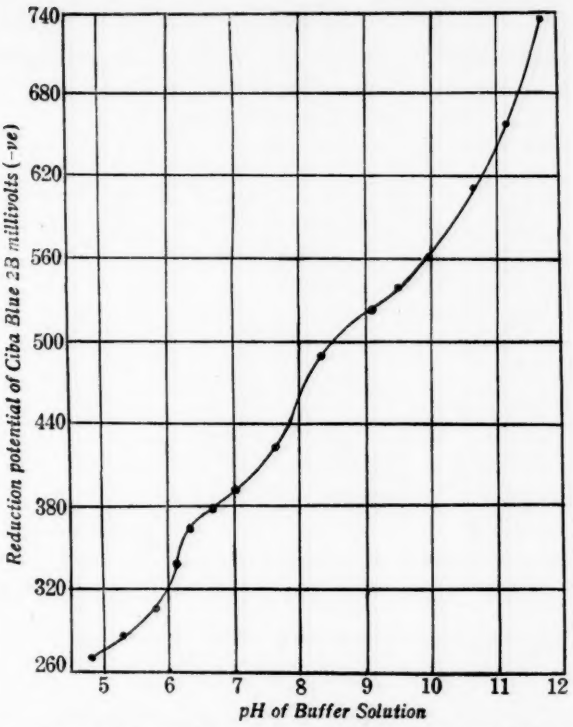


FIG. 4. Relation between pH and the reduction potential of Ciba Blue 2 B

Tables III and IV give the relation between pH and the difference in the oxidation potential of sodium hypochlorite and the reduction potential of the vat dyestuff. The values of the oxidation potentials of sodium hypochlorite are reproduced from Part I of the present communication[3]; the reduction potentials of Cibanone Orange R and Ciba Blue 2 B are taken from Tables I and II respectively. From the two sets of figures the differences are calculated. The relation between this difference and pH is shown graphically in Figs. 5 and 6. It is seen that Cibanone Orange R shows a maximum at pH 7·25 while Ciba Blue 2 B shows it at pH 6·34.

TABLE III

Relation between pH and the difference in oxidation potential of hypochlorite and reduction potential of Cibanone Orange R

pH	Oxidation potentials (millivolts)* (+) A	Reduction potential of Cibanone Orange R (millivolts) (−)B	Difference in millivolts A−(−B)=A+B
10·15	885	583·6	1468·6
9·58	939	558·4	1497·4
9·15	977	525·7	1502·7
8·68	1023	481·7	1504·7
8·02	1081	449·5	1430·5
7·55	1126	433·4	1559·4
7·25	1155	415·7	1570·7
6·95	1173	387·7	1560·7
6·55	1200	359·2	1559·2
6·06	1234	318·7	1552·7
5·92	1241	310·0	1551·0
5·38	1277	302·0	1579·0
4·95	1305	279·3	1584·3

* Reproduced from the paper by Joshi, Mhatre and Nabar, *This Journal*, 1949, **29**, 277.

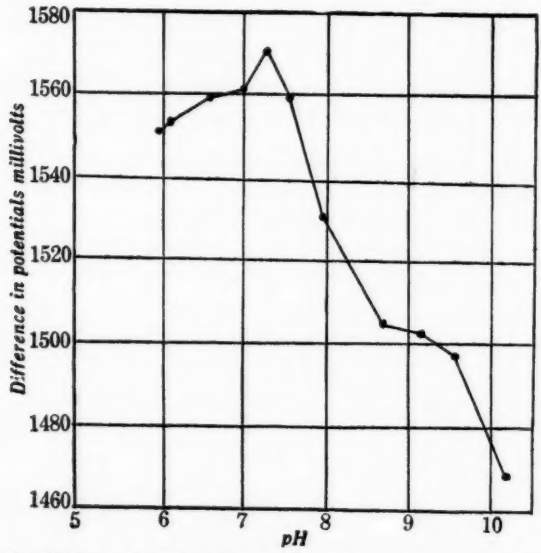


FIG. 5. Relation between pH and difference in the oxidation potential of hypochlorite and reduction potential of Cibanone Orange *R*

TABLE IV

Relation between pH and the difference in the oxidation potential of sodium hypochlorite and the reduction potential of Ciba Blue 2 B

pH	Oxidation potential of hypochlorite (millivolts)* (+) A	Reduction potential of Ciba Blue 2B (millivolts) (−) B	Difference between potentials (millivolts) A−(−B)=A+B
10·00	900	563·0	1463·0
9·55	942	546·8	1488·8
9·15	977	522·3	1499·3
8·36	1050	488·7	1538·7
7·65	1112	423·2	1541·2
7·02	1168	392·3	1560·3
6·72	1188	378·3	1566·3
6·34	1214	364·5	1578·5
6·14	1227	338·0	1565·0
5·83	1248	305·6	1553·6
5·30	1282	287·5	1569·5
4·85	1311	267·3	1578·3

* Reproduced as indicated in Table III.

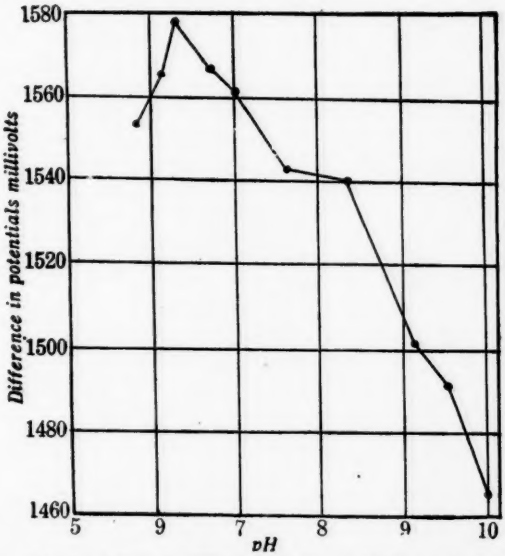


FIG. 6. Relation between pH and difference in the oxidation potential of hypochlorite and reduction potential of Ciba Blue 2 B

The values of oxygen consumption by leuco-Cibanone Orange R and leuco-Ciba Blue 2 B dyed cotton at 30° C. are shown in Tables V and VI respectively and the relation between pH and oxygen consumption is graphically shown in Figs. 7 and 8.

TABLE V

Relation between pH and oxygen consumption (Temp. 30° C.)

(Cibanone Orange R)

pH of buffered sodium hypochlorite solution	Milliatoms of oxygen consumed by 100 g. of dyed cellulose
9·08	7·90
8·90	8·08
7·98	11·02
7·30	20·73
6·91	19·82
6·06	16·91
5·81	12·75
5·32	11·27
4·99	9·02

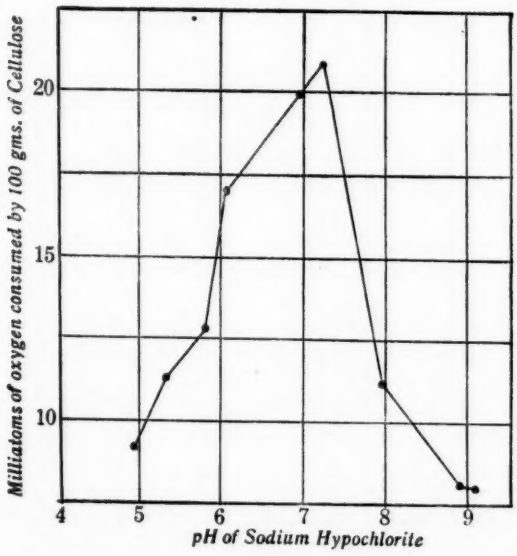


FIG. 7. Relation between pH of sodium hypochlorite solution and oxygen consumed by Cibanone Orange *R*, dyed cotton

TABLE VI

Relation between pH and oxygen consumption (Temp. 30° C.)

(Ciba Blue 2 B)

pH of buffer sodium hypochlorite solution	Milliatoms of oxygen consumed by 100 g. of dyed cellulose
9·056	14·06
8·10	22·28
7·48	23·83
6·99	27·63
6·13	34·21
5·98	29·02
5·40	27·54
4·60	24·70

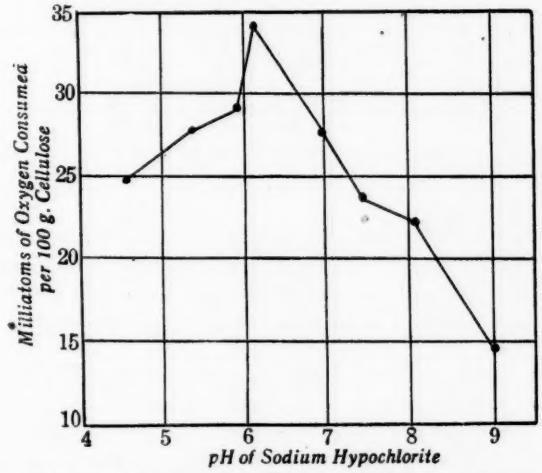


FIG. 8. Relation between pH of sodium hypochlorite solution and oxygen consumed by Ciba Blue 2 B dyed cotton.

It is interesting to find that for Cibanone Orange R, the maximum oxygen consumption takes place at pH 7·3, which is the same as in Fig. 5; and in case of Ciba Blue 2 B, it is at pH 6·34 which is also the maximum point in Fig. 6.

In Fig. 9 is shown the relation between the oxygen consumption and the difference between the potentials for both the dyes. There exists a straight line relationship between the two quantities which indicates that the rate of oxygen transfer is directly proportional to the difference in the potential values.

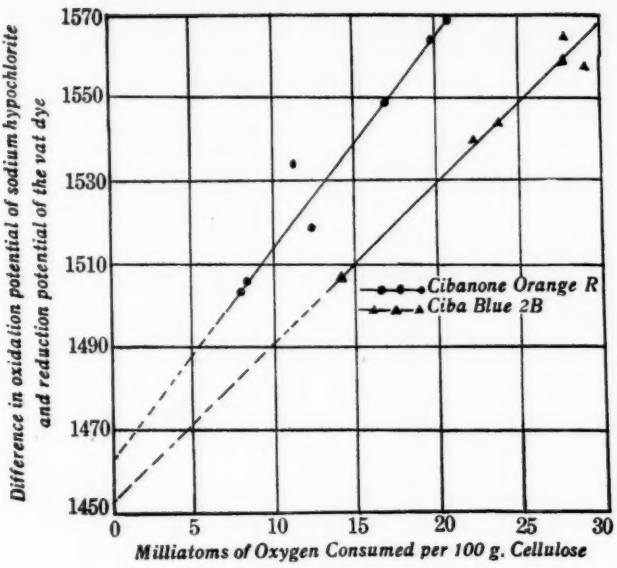


FIG. 9

It is extremely interesting to note that both the straight lines when produced backwards cut the potential axis at about 1,455–1,466 millivolts, indicating that for this difference theoretically no acceleration of the oxidation should occur. Nabar, Scholefield and Turner[2] have also made similar observations.

DISCUSSION

The results described in the foregoing have to be discussed so as to bring out clearly: (*A*) the significance of the electrometric measurements for the system Pt/leuco-vat dyed cotton in air-free buffer solution and (*B*) the mechanism of acceleration of the oxiadtion.

(*A*) *The significance of the electrometric measurements for the system Pt/leuco-vat dyed cotton in air-free buffer solution.*—In considering the theoretical aspects of the potential measurements of the system, Pt/leuco-vat dye-cellulose complex (in air-free buffer solution of known pH value), a number of equilibria, set up as a result of (*a*) the molecular structure of the dye, (*b*) the ease with which it can be reduced and oxidised, and (*c*) the influence of hydrogen-ion concentration on (i) the equilibrium:—Quinone ⇆ Hydroquinone and (ii) the dissociation of the hydroxyl groups of the leuco compound, will have to be considered.

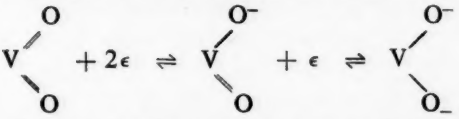
During the change, leuco-vat dye →vat dye, evidence[1, 7, 8] of the formation of an intermediate compound known as semiquinone is available. The stages undergone during the oxidation may be represented as

Hydroquinone		Semiquinone		Quinone
$^{-}O—R—O^{-}$	$\rightleftharpoons$	$^{-}O—R=O + \epsilon$	$\rightleftharpoons$	$O=R=O + 2\epsilon.$
(Leuco-vat dye)		(Intermediate compound)		(Vat dye)

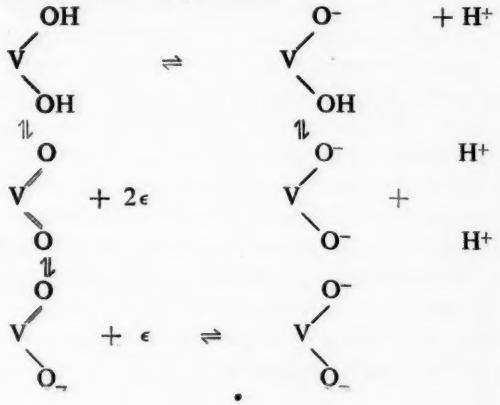
There is also ample evidence[7, 8, 9, 10] to indictae that vat dyes and their leuco-compounds when present together behave identically with many other typical reversible oxidation-reduction systems. If all the forms in which a vat dye can exist are considered as dissolved in the buffer solution and if an indifferent electrode such as platinum is placed in this solution, due to the interchange of electrons, the electrode will acquire a definite charge. The general equation relating to the composition of such a reversible system to the potential set up may be expressed as follows:—

$$E = E_0 + \frac{RT}{nF} ln \frac{[\text{oxidant}]}{[\text{reductant}]}.$$

Apart from the straightforward equilibrium mentioned, *viz.*,



which may be operative in a definite manner at a fixed hydrogen-ion concentration, when one considers it in solutions of different hydrogen-ion concentrations, the system becomes more complicated and under these circumstances, the number of equilibria to be encountered which may influence the actual value of the potential set up at the platinum electrode, may be represented by the following scheme:



Hence the curve relating pH to the reduction potential may not be as simple as to be represented by the equation referred to above. To add to this difficulty, one has to encounter the extremely small solubility of the vat dyes and their leuco-compounds in aqueous medium so that the system, though electrochemically sound, is poorly poised and hence takes a considerably long time to come to a steady value.

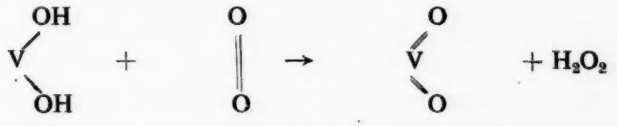
Examination of the curves shown in Figs. 1 and 2 giving relation between the reduction potential and the time of measurement, shows that there is a region which is definitely constant. For alkaline buffers, the potentials slowly rise with time, come to a steady value which remains constant for several minutes and then show a steady fall. On the acid side, however, the potential values show a drop in the beginning, then reach a stable value remaining constant for several minutes and then show a steady fall. Throughout the measurements, these stable values of the potentials have been accepted as the measure of the potential set up at the platinum electrode due to the combined influence of the various equilibria already mentioned.

It is interesting to inquire why the potential values on the acid side first decrease, come to a steady value and fall again, while those on the alkaline side first increase, reach a stable value and then drop. Several factors may be responsible for this behaviour. Firstly, the leuco-dyed cotton, which has been wrapped round the platinum wire, is washed with distilled water, the pH of which is near about the neutral point. When such an electrode in contact with air-free distilled water is placed in an acid buffer, some time is necessary for the acid buffer to diffuse into the cotton and the water into the buffer solution so that an equilibrium buffer mixture is formed. Since the reduction potentials become more and more negative with increasing pH, it is expected that the electrode potential in presence of air-free distilled water (which is approximately neutral in pH) will be higher than what it would be if the electrode were in contact with the acid buffer itself. The slow diffusion of the buffer into the cotton and the consequent displacement of water, causes a fall in the potential until an equilibrium is reached when the potential remains steady. The fall which occurs after the potential has remained steady for several minutes may be due to the slow diffusion of oxygen into the electrode vessel upsetting the equilibrium set up at the electrode. Oxygen might be introduced through tiny leakages in the various connections made to the electrode vessel or through the calomel half cell. On the alkaline side, however, the potentials first rise, indicating that the outside buffer which is of a higher pH value slowly displaces the water until an equilibrium buffer mixture is formed when a stable value is

attained. This is followed by a steady fall, the reasons for which appear to be the same as those advanced above.

The electrometric measurements as described in the foregoing are distinct from those made by Geake and Appleton[8] for vat dyestuffs. They measured the potentials of several vat ⇆ leuco-vat dye systems in presence of aqueous alkaline solutions mixed with pyridine, so that the potentials measured were due to the true equilibrium of the leuco-vat ⇆ vat-dye system.

Examination of the curve in Fig. 3 giving relation between pH and the reduction potential of Cibanone Orange R reveals that there are four distinct inflexions or steps indicating the possibility of the presence of four weakly dissociating acid groups in the molecule. In a leuco-vat dye, these are represented by hydroxyl groups formed during the change Quinone ⇆ Hydroquinone. Similar curve (Fig. 4) for Ciba Blue 2 B shows a definite presence of two inflexions or steps. From the chemical constitution of Ciba Blue 2 B, it is easily seen that it contains two carbonyl groups capable of being reduced to the hydroxyl stage, so that the two inflexions on the pH-reduction potential curve (Fig. 4) confirm the presence of two weakly dissociable acid groups. If this hypothesis is correct, then from what has been said above, Cibanone Orange R, the constitution of which is unknown, may contain four reducible carbonyl groups. This agrees very well with the results obtained by Atherton and Turner[11] on the basis of the reoxidation of leuco-Cibanone Orange R by air and the simultaneous formation of hydrogen peroxide. From the amounts of hydrogen peroxide formed during the reoxidation of leuco-Cibanone Orange R, the above authors on the basis of the reaction



predict the presence of four reducible positions in the dye molecule.

Another interesting feature of the results is the fact that each hydroxyl group dissociates independently of the other and it appears from the distinct steps in the curves (Figs. 3, 4) that unless dissociation of one hydroxyl group is complete, the next hydroxyl group is not affected at all, so that the various hydroxyl groups follow one another until the dye molecule is fully dissociated. It can also be said that the various hydroxyl groups differ with respect to their ionisation constant, since they are progressively dissociating one after the other with increasing pH. It is difficult to state which

of the hydroxyl groups first start functioning. All the same it is clear that each inflexion indicates complete dissociation of one hydroxyl group. This behaviour is quite common with polybasic organic acids.

Hence, apart from the possibility of the actual determination of the reduction potentials of vat dyes from the point of view of their tendering activity, this method might be of use in determining the number of chemically reducible groupings in a vat dyestuff of unknown constitution.

(*b*) *Mechanism of accelaration of the oxidation.*—The most outstanding feature of the results described earlier is the close similarity in the shape of the curve showing relation between pH and oxygen consumption and that of the curve showing relationship of pH to difference between the oxidation potential of sodium hypochlorite solution and reduction potential of vat dyes [Cibanone Orange R (Figs. 7 and 5) and Ciba Blue 2 B (Figs. 8 and 6)].

The pH-oxygen consumption curve (Fig. 7) for Cibanone Orange R shows a maximum at pH 7·3 which is also the maximum point in the curve (Fig. 5) showing the relation between pH and the difference between the oxidation potential of sodium hypochlorite and the reduction potential of Cibanone Orange R. The same similarity as shown in case of Cibanone Orange R exists in the curves in Figs. 8 and 6 for Ciba Blue 2 B also, but is not so complete due to the fact that Ciba Blue 2 B itself is susceptible to attack by sodium hypochlorite.[12] Ciba Blue 2 B undergoes destruction by the action of the hypochlorite solution and the decomposition products thus formed are known to accelerate the decomposition of sodium hypochlorite.[12] In spite of this, however, the maximum points in both the curves coincide at about pH 6·3.

One point of great interest that must be mentioned here is the straight line relationship obtained between the oxygen uptake and the difference between the oxidation potential of hypochlorite and the reduction potential of the vat dyestuff (Fig. 9). This shows that the extent of chemical attack is directly proportional to the difference in the oxidation potential of the hypochlorite and the reduction potential of the vat dye; hence the latter can be considered as the measure of the oxidising intensity.

If the mechanism of oxygen transfer to cellulose in case of both the dyes is the same, one would expect the two straight lines to coincide with one another or at least to be parallel to one another. It is, however, seen that the oxygen loss per millivolt in case of Ciba Blue 2 B is greater than that for Cibanone Orange R. This greater rate of oxygen transfer, as has already been pointed out, must be due to the self-oxidation of Ciba Blue 2 B.[12] The

actual amount of oxygen which is utilized in this reaction is not easy to be determined.

If the straight lines, in Fig. 9 are extended backwards so as to cut the e.m.f. axis, it is found that for Cibanone Orange R the line crosses the axis at an e.m.f. value of about 1,462 millivolts; while the same for Ciba Blue 2 B crosses at about 1,454 millivolts, indicating that for differences in the oxidation potential of hypochlorite and the reduction potential of the reducing substances, below these values, there should be no appreciable acceleration. Even allowing for the very complex system under examination and the experimental error that is likely to occur, it is interesting to find the two values of the potentials in case of both the dyes to be very near to one another. It is equally interesting to recall similar observation recorded by Nabar, Scholefield and Turner,[2] who suggested from similar argument, that at 20° C. for Cibanone Orange R, below 1,483 millivolts, for corrected oxidation potential, no acceleration should take place.

From what has been said above, it may be concluded that the accelerated oxidation is conditioned by the reduction potential of the vat dye present on the fibre. This may not be as simple as it appears since as has already been mentioned in the first part of the discussion, the system is extremely complicated due to the various equilibria operating simultaneously.

It must be pointed out that, while considering the influence of reduced vat dyes in accelerating the rate of cellulose oxidation by hypochlorite solutions, Nabar, Scholefield and Turner[2] suggested that the measure of the tendency of hypochlorite to attack cellulose may not be its oxidation potential alone but the difference between the value of this potential and the reduction potential of the reduced vat dyestuff present on the fibre. The results described in the foregoing substantiate the suggestion.

It is extremely interesting to mention the results obtained by Mhatre and Nabar[4] for $Fe^{\cdot\cdot} \leftrightarrows Fe^{\cdots}$ system on cotton. They showed similar behaviour to exist when $Fe(OH)_2$ deposited on cotton is oxidized to the ferric stage by sodium hypochlorite. The coincidence of the pH value (pH 6·3) for maximum oxygen consumption with that where maximum point is obtained in the curve showing the relation of pH to the difference between the oxidation potential of hypochlorite and the reduction potential of ferrous hydroxide is equally strongly demonstrated by their results.

From what has been said in the foregoing, it is clearly seen that the three reducing substances, namely, leuco-Cibanone Orange R, leuco-Ciba Blue 2 B and Ferrous Hydroxide, when deposited on cotton, influence the

course of oxygen transfer in such a manner that the pH for maximum rate of oxygen transfer to cellulose is not the same in all the three cases. For leuco-Cibanone Orange R, this happens to be at about pH 7·3, while for ferrous hydroxide it is approximately at pH 6·3, which is also the point of maximum oxygen consumption for leuco-Ciba Blue 2 B.

From the various observations recorded above, it is easily seen that the pH for maximum oxygen transfer is different for different reducing substances and that the course of oxygen transfer is determined by the combined effect of the hypochlorite and the reducing substance.

All these observations lead one to think that in presence of substances such as those mentioned above, the hypochlorite looses its identity as far as the rate of oxygen transfer to cellulose is concerned and is solely guided by certain physico-chemical properties of the substances present. As has been demonstrated at least in the three cases, *e.g.*, those of the systems $Fe^{\cdot\cdot} \leftrightarrows Fe^{\cdot\cdot\cdot}$ leuco-Cibanone Orange R $\leftrightarrows$ Cibanone Orange R and leuco-Ciba Blue 2 B $\leftrightarrows$ Ciba Blue 2 B, the reduction potentials as measured by the method described, play an important part in determining the course of oxidation and also the point of maximum oxygen consumption.

References

1. Mhatre, Nabar and Vyas .. *This Journal*, 1950, **32**, 319.
2. Nabar, Scholefield and Turner .. *J. Soc. Dyers and Col.*, 1937, **53**, 5.
3. Joshi, Mhatre and Nabar .. *This Journal*, 1949, **29**, 277.
4. Mhatre and Nabar .. *Nature*, 1947, **159**, 372.
5. Joshi and Nabar .. *Ibid.*, 1947, **159**, 711.
6. C. Doreé .. *Methods of Cellulose Chemistry*, 1947, 4, Chapman and Hall.
7. Geake and Lemon .. *Trans. Farad. Soc.*, 1938, **34**, 1409.
8. ——— and Appleton .. *Ibid.*, 1941, **37**, 45.
9. Conat and Fieser .. *J. Amer. Chem. Soc.*, 1922, **44**, 1382.
10. Waly, Preston, Scholefield and Turner .. *J. Soc. Dyers and Col.*, 1945, **61**, 245.
11. Atherton and Turner .. *Ibid.*, 1946, **62**, 108.
12. Bhujang, Mhatre and Nabar .. *Curr. Sci.*, 1944, **13**, 281.

EVALUATION OF THE SPECIFIC HEAT OF DIAMOND FROM ITS RAMAN FREQUENCIES

By D. Krishnamurti

(From the Raman Research Institute, Bangalore)

Received July 11, 1951

(Communicated by Sir C. V. Raman, N.L.)

1. Introduction

The case of diamond has played a historic role in the development of the theory of specific heats of crystalline solids. Weber in 1875 discovered that the specific heat of diamond shows large variations with temperature, falling off and tending towards small values when the temperature is lowered and on the other hand increasing when it is raised, and tending towards the limiting value given by Dulong and Petit's law, above 1,000° C. The specific heat of diamond has been further investigated by various authors in more recent times. It will suffice here to mention the work of Magnus and Hodler (1926) which covers the range 273°–1,100° K at intervals of 50° and that of Pitzer (1938) who made a series of determinations in the low temperature range between 70° K and 300° K.

In his celebrated paper introducing the quantum theory of specific heats, Einstein (1907) showed that Weber's data are in fair accord with a specific heat curve calculated on the assumption that the carbon atoms in diamond have a single vibration frequency corresponding to an infra-red wavelength of 11 μ. Subsequently, when more precise experimental data became available, other attempts were made to fit them into a specific heat formula based on different assumptions regarding the nature of the vibration spectrum of diamond. It cannot be said that any of these theories has been really successful in explaining the observed facts. The best-known amongst these theories is that due to Debye. Pitzer found that the variations of the specific heat in the range of temperatures examined by him could not be fitted into a single expression of the Debye type. He calculated the " characteristic temperatures " from the observed specific heat at 70·16 °, 125·28° and 231·06° K and found them as 1930°, 1874° and 1817 ° K respectively. Reversing the process and calculating the specific heat from these different values, it will be seen from the figures in Table I below that the calculated and observed specific heats differ from each other by as much as 10% to 20%.

To possess real significance, a specific heat formula should be based on *independent* knowledge of the vibration spectrum of the substance under study. Fortunately, in the case of diamond, such knowledge has come to hand from spectroscopic investigations by several different methods. The most precise data are those derived from Raman effect studies. It is proposed in the present paper to present calculations of the specific heat of diamond made on the basis of the spectroscopically known vibration frequencies of the structure of the crystal.

TABLE I

Temp.° K	Calc. C_v $\theta=1930$	Calc. C_v $\theta=1874$	Calc. C_v $\theta=1817$	Observed C_v
70·16	0·0224	0·0244	0·0268	0·0224
125·28	0·127	0·138	0·152	0·138
231·06	0·738	0·796	0·858	0·858

2. THE VIBRATION SPECTRUM OF DIAMOND

Many investigations have been made on the Raman effect in diamond. It will suffice here to mention the early work of C. Ramaswamy (1930) and the latest investigations of R. S. Krishnan (1947) and P. S. Narayanan (1951). C. Ramaswamy discovered the first order spectrum which consists of a single intense sharp line of frequency shift 1332 cm.$^{-1}$, while the latter authors have found a series of intense and sharp lines and interpreted them as the overtones and combinations of the fundamental vibration frequencies. The basis for this interpretation is the theory of lattice dynamics put forward by Sir C. V. Raman (1943, 1947). Exact expressions for the frequencies of the modes of vibration indicated by the theory have been found and evaluated by K. G. Ramanathan (1947). They give data in satisfactory accord with the experimentally observed frequencies. These are eight in number and have the following values expressed in wave numbers; their respective degeneracies indicated by the theory are shown enclosed in brackets.

1332 (3), 1250 (8), 1232 (6), 1149 (4),

1088 (6), 1008 (4), 752 (6), 620 (8).

Totalling the numbers appearing within brackets, we account for 45 out of the 48 degrees of freedom of the 16 atoms contained in eight contiguous cells of the crystal structure. The remaining three degrees of freedom refer respectively to the three trasnlations of the group of 16 atoms and are identifiable with the movements of the volume element containing this group and associated with vibrations of the elastic solid type.

If N be the number of atoms in the atomic volume V of the crystal, the degrees of freedom associated with the elastic modes of vibration are thus $\frac{3N}{16}$ in number. We assume these to be equally distributed over the three classes of elastic wave-patterns possible in a crystal. It is necessary to determine how these degrees of freedom are distributed over the possible frequency range in each case. The modes of stationary elastic vibration as well as their frequencies would evidently depend upon the velocities of wave-propagation in different directions. For the purpose of our calculations, we shall assume that the frequency distribution for each of the three classes of waves is the same as for an isotropic solid in which the velocity of propagation is the mean velocity obtained by averaging over all possible directions within the crystal.

3. Evaluation of the Specific Heat

The limiting frequency $\nu_i\,(i=1, 2, 3)$ for the longitudinal and the two transverse waves is given by $\nu_i=\left(\frac{3N}{64\pi V}\right)^{\frac{1}{3}}W_i$ where W_i is the average velocity of the particular type of wave. Therefore the specific heat is given by

$$C_v=3R\sum_1^8\sigma_s\,E\left(\frac{h\nu_s}{kT}\right)+\frac{3R}{48}\sum_{i=1,2,3}D\left(\frac{h\nu_i}{kT}\right),$$

where E and D are respectively the Einstein and Debye functions, σ_s the weight factor for frequency ν_s, which can be obtained from the degeneracy.

The velocities in the 26 directions given by the six cubic, eight octahedral and twelve dodecahedral directions are taken and the average for each type of the waves is found. The velocities in these directions can be obtained from the well-known cubic equation in terms of the elastic constants which have been evaluated by the present author (1951), and the following values are found for ν_1, ν_2 and ν_3.

$$\nu_1=824\text{ cm.}^{-1};\quad \nu_2=497\text{ cm.}^{-1};\quad \nu_3=455\text{ cm.}^{-1}$$

4. The Specific Heat at Low Temperatures

Table II shows the specific heat calculated by the present method and compared with the experimental results of Pitzer. Pitzer himself states that his experimental values may be in error by as much as 5% at the lowest of temperatures and that the possible errors are quite small at about 150° K, but might again be larger towards the upper end of the temperature range. It is noticed also that in the latter part of the range, several of Pitzer's observational points fall out of the smooth graph reproduced in his paper by 1% or more. Examined in the light of these remarks, the differences

TABLE II

Temp.° K	Optical frequencies	Elastic spectrum	Total C_v	Observed C_v	Percentage Difference
70·16	0·0005	0·0224	0·0229	0·0224	+2·2
75·37	0·0010	0·0273	0·0283	0·0296	−4·4
81·59	0·0024	0·0338	0·0362	0·0362	0
88·65	0·0048	0·0418	0·0466	0·0452	+3·1
96·68	0·0096	0·0517	0·0613	0·0592	+3·5
105·1	0·0165	0·0625	0·0790	0·0785	+0·6
113·04	0·0282	0·0732	0·1014	0·0991	+2·3
125·28	0·052	0·090	0·142	0·138	+2·9
134·29	0·076	0·102	0·178	0·174	+2·3
144·1	0·107	0·115	0·222	0·218	+1·8
153·71	0·144	0·128	0·272	0·267	+1·9
162·76	0·185	0·139	0·324	0·318	+1·9
173·33	0·237	0·152	0·389	0·386	+0·8
181·96	0·286	0·161	0·447	0·444	+0·7
191·44	0·330	0·172	0·502	0·518	−3·1
200·94	0·405	0·182	0·587	0·595	−1·3
211·84	0·481	0·193	0·674	0·685	−1·6
231·06	0·628	0·210	0·838	0·858	−2·3
241·09	0·709	0·218	0·927	0·918	−1·0
252·37	0·804	0·227	1·031	1·033	−0·2
264·31	0·907	0·236	1·143	1·137	+0·5
276·61	1·016	0·244	1·260	1·257	+0·2
287·96	1·105	0·251	1·356	1·355	+0·1

between the observed and calculated values, which are shown as a percentage in the last column of Table II are not larger than might reasonably be expected. It may therefore be claimed that the theory gives a satisfactory account of the facts. This agreement is all the more significant when it is remembered that the theoretical calculations are completely independent and do not make use of the specific heat data themselves.

Table III shows the calculation of the specific heat on the lines indicated by Dayal (1944), in which the acoustic spectrum is represented by one single

TABLE III

Temp.° K	Optical Frequencies	Elastic Spectrum	Total C_v	Observed C_v	Percentage Difference
70·16	0·0005	0·0230	0·0235	0·0224	+4·9
81·59	0·0024	0·0349	0·0373	0·0362	+3·0
105·1	0·0165	0·0668	0·0833	0·0785	+6·1
125·28	0·0519	0·0975	0·1494	0·1380	+8·3
162·8	0·1845	0·1540	0·3385	0·3180	+6·5

cut-off frequency at 525 cm.$^{-1}$ which was calculated after finding the mean velocity according to the interpolation method due to Hopf and Lechner (1914). The agreement with the experimentally observed values is seen to be much less satisfactory than in Table II.

5. The Specific Heat at High Temperatures

Table IV gives the calculated values compared with the experimental values of Magnus and Hodler. Here again, the theory gives results in excellent agreement with the observations over the whole range of temperature

TABLE IV

Temp.° K	Optical Frequencies	Elastic Spectrum	Total C_v	Observed C_v	Percentage Difference
273	0·984	0·241	1·225	1·252	−2·2
300	1·217	0·258	1·475	1·520	−3·0
350	1·688	0·281	1·969	1·985	−0·8
400	2·128	0·298	2·426	2·411	+0·6
450	2·526	0·312	2·838	2·798	+1·4
500	2·883	0·322	3·205	3·149	+1·8
550	3·191	0·330	3·521	3·465	+1·6
600	3·460	0·336	3·796	3·749	+1·3
650	3·686	0·341	4·027	3·999	+0·7
700	3·890	0·345	4·235	4·222	+0·3
750	4·065	0·348	4·413	4·414	−0·02
800	4·216	0·351	4·567	4·580	−0·3
850	4·342	0·353	4·695	4·717	−0·5
900	4·452	0·355	4·807	4·833	−0·5
950	4·557	0·357	4·914	4·923	−0·2
1000	4·646	0·358	5·004	4·992	+0·2
1050	4·724	0·359	5·083	5·030	+1·05
1100	4·794	0·361	5·155	5·060	+1·9

from 350° K to 1100° K. At the two lowest temperatures (273° and 300° K) there is a sensible discrepancy, but on a comparison of the data of Magnus and Hodler with those of Pitzer in the region where they overlap, it becomes clear that such discrepancy arises from errors in the experimental data.

Though the eight fundamental vibration frequencies show a sensible variation with temperature, such variation does not noticeably influence the calculated values of the specific heat, especially at the lower temperatures. A calculation made for the temperature 900° K taking such variations into account gives C_v as 4·831, while the values obtained without taking it into account is 4·807.

In conclusion, the author expresses his sincere thanks to Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting this problem and the inspiring guidance that he have during the course of this investigation.

6. Summary

The specific heat of diamond is evaluated from the knowledge of its vibration spectrum obtained principally from Raman effect studies. The vibration spectrum is known to consist of eight discrete monochromatic frequencies followed by a continuous spectrum of elastic vibrations. Accordingly, the specific heat is expressed as the sum of eight Einstein functions, supplemented by three Debye functions representing respectively the three types of elastic vibration possible in the crystal. A close agreement is found between the calculated and the experimental values over the entire range of temperatures between 70° K and 1100° K, which is all the more significant in view of the calculations being completely independent of the specific heat data themselves.

References

1. Dayal, B. .. *Proc. Ind. Acad. Sci.*, 1944, **19**, 224.
2. Einstein, A. .. *Ann. der. Physik.*, 1907, **22**, 180.
3. Hopf and Lechner .. *Ber. Deutsch. Phys. Ges.*, 1914, 643.
4. Krishnamurti, D. .. *Proc. Ind. Acad. Sci.*, 1951, **33**, 325.
5. Krishnan, R. S. .. *Nature*, 1947, **159**, 60.
6. ———— .. *Proc. Ind. Acad. Sci.*, 1947, **26**, 399.
7. Magnus and Hodler .. *Ann. der. Physik.*, 1926, **80**, 808.
8. Narayanan, P. S. .. *Proc. Ind. Acad. Sci.*, 1951, **34**, 1.
9. Pitzer, K. S. .. *J. Chem. Phys.*, 1938, **6**, 68.
10. Raman, C. V. .. *Proc. Ind. Acad. Sci.*, 1943, **18**, 237.
11. ———— .. *Ibid.*, 1947, **26**, 356.
12. Ramanathan, K. G. .. *Ibid.*, 1947, **26**. 481.
13. Ramaswamy, C. .. *Nature*, 1930, **125**, 704.
14. ———— .. *Ind. Jour. Phys.*, 1930, **5**, 97.
15. Weber .. *Phil. Mag.*, 1875, **49**, 161.

THE THEORY OF OPTICAL ACTIVITY OF CRYSTALS

III. Calculation of the Rotatory Power of β-Quartz

By G. N. Ramachandran, F.A.Sc.

(*From the Department of Physics, Indian Institute of Science, Bangalore* 3)

Received June 7, 1951

1. Introduction

In Parts I and II (author, 1951 *a*, *b*), the general principles of the theory were discussed and they were applied to the cases of $NaClO_3$ and $NaBrO_3$ to calculate the rotatory power. These two crystals belong to the cubic system and their optical activity could be defined by one parameter. A hypothetical uniaxial crystal having a spiral structure (point-group D_4) was also considered in Part I, for which it was shown that the optical activity both along and at right angles to the optic axis could be calculated, provided the optical anisotropies of the individual atoms were known. The results obtained in this case were promising, since the rotation at right angles to the axis was found to be of opposite sense to that along the axis, a fact observed for α-quartz (Bruhat and Grivet, 1935). In this paper, therefore, we consider the case of β-quartz.

The rotatory power along the optic axis has been measured for both α- and β-quartz at various temperatures (Sosman, 1927) while that at right angles to the optic axis has only been measured for α-quartz at room temperature (Bruhat and Grivet, *loc. cit.*). However, the structures of the two modifications are very similar, there being only a slight alteration in the positions of the oxygen atoms at the transition temperature, which changes the point-group symmetry from D_3 of α-quartz to D_6 of β-quartz. Also the optical properties exhibit only small changes of the order of 5% at the transition temperature. Therefore, the values for the rotatory power are not likely to differ appreciably between α- and β-quartz. However, it is more convenient to make calculations for β-quartz, as it belongs to the higher hexagonal point-group, there being thus less independent parameters to consider. Consequently, the calculations have only been made for the hexagonal modification.

The structure of β-quartz has been determined by Bragg and Gibbs (1925). It belongs to the space-group $D_6^4 - C6_22$ and the enantiomorphous

space-group D_6^5– $C6_42$ and the co-ordinates of the Si and O atoms are given below, there being 3 SiO_2 atoms per unit cell.

Si	$\frac{1}{2}, 0, 0$	$-\frac{1}{2}, -\frac{1}{2}, \frac{1}{3}$	$0, \frac{1}{2}, \frac{2}{3}$
O	$u, \bar{u}, -\frac{1}{6}$	$\bar{u}, 2\bar{u}, \frac{1}{2}$	$2\bar{u}, \bar{u}, \frac{1}{6}$
	$\bar{u}, u, -\frac{1}{6}$	$u, 2u, \frac{1}{2}$	$2u, u, \frac{1}{6}$.

with $u=0{\cdot}21$. The unit cell dimensions are $a=5{\cdot}01$ A, $c=5{\cdot}47$ A, $c/a=1{\cdot}09$. A projection of the structure on the basal c plane is shown in Fig. 1, in which the numbers denote the heights of the atoms above the plane through the origin, in units of $c/6$. The arrows indicate how the atoms are linked up; they form left-handed spirals progressing upwards in the direction of the arrows. We denote by OA, OB, OC the hexagonal axes. However, for making calculations, it is preferable to choose the orthogonal set of axes Ox, Oy, Oz shown in Fig. 1. If x', y', z' are the co-ordinates of an

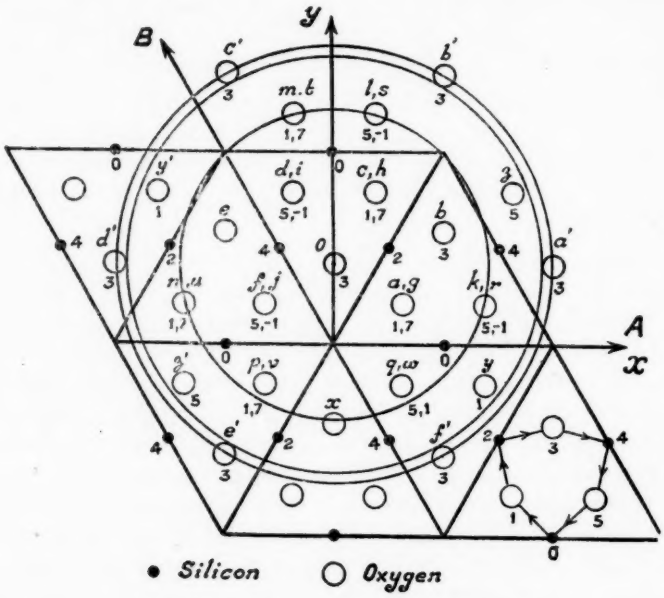


FIG. 1. Atomic structure of β–quartz

atom in the hexagonal system of axes, then the co-ordinates x, y, z with respect to the rectangular system are given by

$$x=x'-y'/2,\ y=\sqrt{3}\,y'/2,\ z=z'.$$

2. Polarisabilities of Silicon and Oxygen Atoms

We may take for the molar refractions the values $R_O = 3{\cdot}56$ and $R_{Si} = 0{\cdot}1$ given by Fajans and Joos (1924). The molar refraction of oxygen is thus of the same order as the value in $NaClO_3$ or calcite. As in Part II, we shall make the simplification of neglecting the polarisability of silicon and assume that the optical properties of quartz are solely determined by the oxygen atoms. This is justified since, according to the above values, silicon contributes only about 1% to the molar refraction of SiO_2.

It is now necessary to estimate the anisotropy of an oxygen atom in the structure. In quartz, each oxygen atom is linked to two silicon atoms, the two bonds being nearly at the tetrahedral angle, as is found in oxygen compounds such as water. The following indirect method may therefore be employed for estimating the anisotropy of oxygen. If one examines a table of depolarisation values ($\triangle$) in light-scattering (*e.g.*, Bhagavantam, 1940, p. 54), it is found that $\triangle$ is generally in the neighbourhood of 1·5% for oxygen components such as water, alcohols, ethers, etc. From this, we can estimate the anisotropy β, which may be defined by

$$\beta^2 = [(a_1-a_2)^2 + (a_2-a_3)^2 + (a_3-a_1)^2]/2a^2, \qquad (1)$$

where a_1, a_2, a_3 are the principal polarisabilities and $a = (a_1 + a_2 + a_3)/3$ is the mean polarisability. β is related to $\triangle$ by the formula

$$\beta^2 = 45\ \triangle/(6 - 7\ \triangle) \qquad (2)$$

(Bhagavantam, 1940), so that, if $\triangle = 0{\cdot}015$, $\beta^2 = 0{\cdot}115$. This value alone is insufficient to fix uniquely $a_1 : a_2 : a_3$. If we assume, in addition, that the molecule has an axis of symmetry, and say $a_2 = a_3$, then a_1/a_2 can be uniquely estimated. Obviously, no such symmetry axis exists for an oxygen atom linked to two groups at 109° 28′. But, we can still estimate a_1, a_2, a_3 by the following method.

It is clear that the effect of a covalent bond would be to pull out the electron distribution of the oxygen atom towards the group to which it is bound. As an idealised case, imagine the bonded oxygen atom to consist of an isotropically polarisable core (O) with polarisability γ and two electron

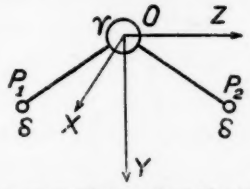


Fig. 2. Axes of polarisability ellipsoid of an oxygen atom

concentrations at P_1 and P_2 with polarisability δ each, the angle P_1OP_2 being 109° 28′ (Fig. 2). Obviously, the principal axes of the polarisability ellipsoid of the whole group would be along OX, OY, OZ. By working out the values of the principal polarisabilities α_1, α_2, α_3 it can be shown that

$$\alpha_1 < \alpha_3 < \alpha_2 \tag{3}$$

The exact values of the ratios $\alpha_1 : \alpha_2 : \alpha_3$ is immaterial, as it would depend very much on the electron distribution, but the above inequalities would be maintained. In the absence of any further data except the value of β and the relation (4), we may assume that

$$\alpha_1 : \alpha_2 : \alpha_3 = 1 : 1{\cdot}5 : 1{\cdot}25 \tag{5}$$

This makes $\beta = 0{\cdot}12$, which is sufficiently close to the value 0·115 calculated from the depolarisation.

Assuming Fajans and Joos' value given earlier for the mean atomic refraction of oxygen, the values of the principal polarisabilities are found to be

$$\alpha_1 = 1{\cdot}419,\ \alpha_2 = 2{\cdot}129,\ \alpha_3 = 1{\cdot}774 \times 10^{-23}. \tag{6}$$

3. Calculation of the Refractive Indices

The general theory of Part I contains, in essence, the formalism required for calculating both the refractive index and the rotatory power and it can be used to calculate the two refractive indices of quartz. However, unlike sodium chlorate, in which the distances between the oxygen atoms in an O_3 group is small compared with the distance between neighbouring groups, the atoms in quartz form an extended structure. The influence of the near neighbours on the refraction of an oxygen atom is therefore appreciable and a larger number of neighbours have to be taken into account for obtaining an accurate result. We shall include all the oxygen atoms occurring within 5 Å of any particular atom in our calculations. There are 33 such and they are indicated by letters a, b, ... e', f' in Fig. 1. The three circles indicate the areas within which the projections of the neighbours should lie if they are in levels 3; (1, 5); (−1, 7) respectively, for them to be within 5 Å from atom O. The distances (R) of the various neighbours and also the values the quantities $p = (3x^2 - R^2)/R^5$, $q = (3y^2 - R^2)/R^5$, $r = (3z^2 - R^2)/R^5$, $s = 3xy/R^5$, $t = 3yz/R^5$, $u = 3zx/R^5$ are shown in Table I. The entries under column 2 will be clear a little later.

The components of the polarisability ellipsoid of the oxygen atom O (with respect to the rectangular system of axes $Oxyz$ of Fig. 1) can be obtained from the values of α_1, α_2, α_3 given above and the configuration of the

TABLE I

Atom	Type	R	p	q	r	s	t	u
b	A_2	2·598	+·101900	−·044920	−·057010	+·043740	..	..
c	A_2	2·598	+·101900	−·044920	−·057010	+·043740	..	..
x	A_2	3·647	−·001030	+·002060	−·001030	..	..	..
a'	A_1	5·010	+·015903	−·007952	−·007952	..	..	..
d'	A_1	5·010	+·015903	−·007952	−·007952	..	..	..
b'	A_1	5·010	−·019900	+·009941	−·007952	+·001032	..	..
c'	A_1	5·010	−·019900	+·009941	−·007952	−·001032	..	..
e'	A_1	5·010	−·019900	+·009941	−·007952	+·001032	..	..
f'	A_1	5·010	−·019900	+·009941	−·007952	−·001032	..	..
a	C_1	2·578	+·007250	−·036450	+·029190	−·037920	+·043800	−·075810
f	B_1	2·578	+·007250	−·036450	+·029190	+·037920	−·043800	−·075810
c	C_2	2·598	−·035240	+·008090	+·027160	+·036620	−·074010	−·0428·0
d	B_2	2·598	−·035240	+·008090	+·027160	−·036620	+·074010	−·042810
g	C_1	4·076	−·008121	−·012535	+·020656	−·003830	−·008853	+·015317
j	B_1	4·076	−·008121	−·012535	+·020656	+·003830	+·008853	+·015317
h	C_2	4·091	−·012467	−·007946	+·020413	+·003927	+·015448	+·008936
i	B_2	4·091	−·012467	−·007946	+·020413	−·003927	−·015448	+·008936
k	B_1	3·990	+·019240	−·013330	−·005913	−·009322	−·004953	+·018539
n	C_1	3·990	+·019240	−·013330	−·005913	+·009322	+·004953	+·018539
l	B_1	3·991	−·013270	+·019198	−·005935	+·009471	+·018623	+·005038
m	C_1	3·991	−·013270	+·019198	−·005935	−·009471	−·018623	+·005038
p	C_2	3·645	−·009054	+·014213	−·005159	+·020094	+·023245	+·013395
q	B_2	3·645	−·009054	+·014213	−·005159	−·020094	−·023245	+·013395
r	B_1	5·089	+·002757	−·006856	+·004102	−·002751	+·002951	−·010996
u	C_1	5·089	+·002757	−·006856	+·004102	+·002751	−·002951	−·010996
s	B_1	5·090	−·006826	+·002733	+·004093	+·002789	−·010964	−·002967
t	C_1	5·090	−·006826	+·002733	+·004093	−·002789	+·010964	−·002967
v	C_2	4·824	−·006052	−·000318	+·006366	+·004953	−·011453	−·006603
w	B_2	4·824	−·006052	−·000318	+·006366	−·004953	+·011453	−·006603
y	C_2	4·750	+·005262	−·000054	−·005208	−·011630	+·006178	−·007752
z'	B_2	4·750	+·005262	−·000054	−·005208	+·011630	−·006178	−·007752
y'	C_2	4·749	+·011348	−·006139	−·005209	−·008115	−·003624	+·009231
z	B_2	4·749	+·011348	−·006139	−·005209	+·008115	+·003624	−·009231

Si–O–Si bonds in the structure. They are calculated to be

$$\left.\begin{aligned} a_{11}^0 &= 1\cdot539\times10^{-23} & a_{23}^0 &= 0 \\ a_{22}^0 &= 2\cdot129\times10^{-23} & a_{31}^0 &= -0\cdot170\times10^{-23} \\ a_{33}^0 &= 1\cdot654\times10^{-23} & a_{12}^0 &= 0 \end{aligned}\right\} \qquad (7)$$

The components of the polarisability ellipsoid of the five other oxygen atoms in the unit cell can be readily obtained from these by the application of suitable symmetry operations. Calling atom O to be of type A_1 and the others respectively of types A_2, B_1, B_2, C_1, C_2 the various components are given in Table II. In this table of transformations, the most general case is considered of a tensor L, which is not necessarily symmetric. Owing to the fact that a two-fold axis along O*y* passes through atom O, there can only be 5 non-vanishing components for this atom, *viz.*,

$$L_{11}=a,\ L_{22}=b,\ L_{33}=c,\ L_{13}=d,\ L_{31}=e.$$

Table II contains all the components of the other atoms in terms of these. Column 2 of Table I gives the type of each atom.

TABLE II

Component	A_1	A_2	B_1	B_2	C_1	C_2
L_{11} ..	a	a	$\frac{1}{4}a+\frac{3}{4}b$	$\frac{1}{4}a+\frac{3}{4}b$	$\frac{1}{4}a+\frac{3}{4}b$	$\frac{1}{4}a+\frac{3}{4}b$
L_{22} ..	b	b	$\frac{3}{4}a+\frac{1}{4}b$	$\frac{3}{4}a+\frac{1}{4}b$	$\frac{3}{4}a+\frac{1}{4}b$	$\frac{3}{4}a+\frac{1}{4}b$
L_{33} ..	c	c	c	c	c	c
L_{23} ..	0	0	$\frac{\sqrt{3}}{2}d$	$-\frac{\sqrt{3}}{2}d$	$-\frac{\sqrt{3}}{2}d$	$\frac{\sqrt{3}}{2}d$
L_{32} ..	0	0	$\frac{\sqrt{3}}{2}e$	$-\frac{\sqrt{3}}{2}e$	$-\frac{\sqrt{3}}{2}e$	$\frac{\sqrt{3}}{2}e$
L_{31} ..	e	$-e$	$\frac{1}{2}e$	$-\frac{1}{2}e$	$\frac{1}{2}e$	$-\frac{1}{2}e$
L_{13} ..	d	$-d$	$\frac{1}{2}d$	$-\frac{1}{2}d$	$\frac{1}{2}d$	$-\frac{1}{2}d$
L_{12} ..	0	0	$\frac{\sqrt{3}}{4}(a-b)$	$\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$
L_{21} ..	0	0	$\frac{\sqrt{3}}{4}(a-b)$	$\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$	$-\frac{\sqrt{3}}{4}(a-b)$

From (9) and (11) of Part I, we have the following equations for the atom O, when the electric vector is E_x, if we neglect the phase changes. (As was mentioned in the earlier parts, it is necessary to take the phase changes into account only for calculating the rotation, but not for calculating the refractive index. This is so because $\cos 2\pi R_j/\lambda_0 \simeq 1$ for all the neighbours that are considered, the error introduced by putting it equal to unity being only of the order of in 10^{-6}.)

$$\mu_{x0}=\alpha_{11}^{0}\left(E_x+\frac{P_x}{3}+F_{x0}\right)+\alpha_{12}^{0}F_{y0}+\alpha_{13}^{0}F_{z0}, \text{ etc.} \qquad (9)$$

where

$$F_{x0} = \frac{1}{4\pi} \Sigma_j (\mu_{xj} p_j + \mu_{yj} s_j + \mu_{zj} u_j), \text{ etc.} \tag{10}$$

Suppose we write

$$\mu_0(\mu_{x0}, \mu_{y0}, \mu_{z0}) = L_0 \ (E + P/3), \tag{11}$$

where the tensor L has five non-vanishing components, say a, b, c, d, e as in (8). Then substituting the numerical values of $\alpha_{11}^0, \ldots$. from (7) and $p_j, \ldots$. from Table II one obtains the following simultaneous equations:

$$\left.\begin{aligned}
0{\cdot}75310\,a - 0{\cdot}10728\,b + 0{\cdot}04128\,d &= \ \ 1{\cdot}539 \times 10^{-23} \\
0{\cdot}06014\,a + 0{\cdot}15807\,b + 0{\cdot}89630\,d &= -0{\cdot}170 \quad ,, \\
0{\cdot}10728\,a + 1{\cdot}13096\,b + 0{\cdot}21566\,d &= \ \ 2{\cdot}129 \quad ,, \\
0{\cdot}97235\,c + 0{\cdot}20372\,e &= \ \ 1{\cdot}654 \quad ,, \\
0{\cdot}18810\,c + 0{\cdot}95320\,e &= -0{\cdot}170 \quad ,,
\end{aligned}\right\} \tag{12}$$

which, on solving, give

$$a = 2{\cdot}251,\ b = 1{\cdot}239,\ c = 1{\cdot}813,\ d = -0{\cdot}559,\ e = -0{\cdot}536 \times 10^{-23}. \tag{13}$$

Adding up the components for the six atoms in the unit cell (of volume V) in the particular cases when the incident electric vector is E_x and E_z, we have

$$\left.\begin{aligned}
P_x &= \frac{\Sigma \mu_x}{V} = \frac{3(a+b)}{V}\left(E_x + \frac{P_x}{3}\right) \\
P_z &= \frac{\Sigma \mu_z}{V} = \frac{6c}{V}\left(E_z + \frac{P_z}{3}\right)
\end{aligned}\right\} \tag{14}$$

Since $P_x/E_x = n_\omega^2 - 1$ and $P_z/E_z = n_\epsilon^2 - 1$,

$$n_\omega = 1{\cdot}500, \quad n_\epsilon = 1{\cdot}522 \tag{15}$$

The experimental values are 1·533 and 1·541 respectively. It is seen that $n_\epsilon > n_\omega$ as found from experiment. The absolute values are, however, smaller by about 1 to 2%, which is of the order of error to be expected due to the omission of the effects of silicon atoms in the calculations. The calculated birefringence is much larger than is observed, 0·02 as against 0·008, but this agreement itself must be considered excellent, as it is much better than the agreement obtained by Bragg (1924) in calcite and aragonite.

4. Calculation of the Rotatory Power

We now consider the phase differences of the incident wave for various atoms in the structure and thus proceed to evaluate the rotatory power.

(*a*) *Propagation along the optic axis Oz.*—It is necessary to calculate the total moment induced in the six atoms in the unit cell along the *y*-axis when the electric vector is along O*x*. Because of the 6-fold axis of symmetry, it can be shown that the mean induced moment along O*y* of all the atoms in the unit cell, when the incident electric vector is along O*x*, is the same as the mean of the perpendicularly induced moments of any particular atom (say O of Fig. 3) when the incident electric vector is along O*x* and O*y*. Consequently, we only make the latter calculation. For an electric vector E_x,

$$\mu_{y0} = \left(E_x + \frac{P_x}{3}\right) \Sigma_j \exp(-2\pi i z_j/\lambda)[L_{11}^{j}(p_j a_{12} + u_j a_{22} + t_j a_{23}) + L_{12}^{j}(u_j a_{12} + q_j a_{22} + s_j a_{23}) + L_{13}^{j}(t_j a_{12} + s_j a_{22} + r_j a_{23})]$$
$$= iK_1(E_x + P_x/3) \quad \text{(say)} \tag{13}$$

Similarly, for incident E_y,

$$\mu_{x0} = iK_2(E_y + P_y/3) \quad \text{(say)} \tag{14}$$

Actual calculations give $K_1 = -3{\cdot}639 \times 10^{-4} n_\omega$, $K_2 + 1{\cdot}480 \times 10^{-4} n_\omega$, so that $(K_1 + K_2)/2 = -1{\cdot}080 \times 10^{-4} n_\omega$.

From these,

$$\frac{P_y}{P_x} = \frac{ig_{33}}{n_\omega^2 - 1} = -i \times (1{\cdot}080 \times 10^{-4}/1{\cdot}745)\, n_\omega$$

and $g_{33}/n_\omega = -7{\cdot}72 \times 10^{-5}$. Therefore, the rotatory power along the optic axis is

$$\rho_\parallel = \frac{\pi}{\lambda} \frac{g_{33}}{n_\omega} = -236^\circ. \tag{16 a}$$

(*b*) *Propagation at right angles to the optic axis.*—Just as in case (*a*), it can be readily shown that the mean value of the perpendicularly induced moment for all the atoms in the unit cell is the mean of the values for any one atom (say 0) for direction of propagation along O*x* and O*y*. Writing $\mu_\perp = -iK_3(E_z + P_z/3)$ for the former and $iK_4(E_z + P_z/3)$ for the latter, we get

$$K_3 = +4{\cdot}196 \times 10^{-4} \bar{n}, \quad K_4 = -3{\cdot}142 \times 10^{-4} \bar{n}$$

so that $(K_3 + K_4)/2 = 0{\cdot}527 \times 10^{-4} \bar{n}$, where $\bar{n} = (n_\omega + n_\epsilon)/2$.

From these, $g_{11}/\bar{n} = +3{\cdot}76 \times 10^{-5}$ and

$$\rho_\perp = \frac{\pi}{\lambda} \frac{g_{11}}{\bar{n}} = +115^\circ \tag{16 b}$$

Thus

$$\rho_\perp/\rho_\parallel = -0{\cdot}487. \tag{17}$$

5. Discussion

The above results may be compared with experiment. As mentioned earlier, data are available only for $\rho_\parallel$ which is 252°/cm. This agrees well with the calculated value of 236°. For α-quartz, $\rho_\perp/\rho_\parallel = -0{\cdot}50$, which is very nearly the same as the value obtained above.

It is interesting to note that the sense of optical rotation is the same as the sense of the spiral in the structure. We have considered in this paper a left-handed spiral, *i.e.*, the spiral progresses towards the observer when turned clockwise. $\rho_\parallel$ in this case is negative, *i.e.*, the rotation is clockwise as the light beam advances towards the observer. However, as was mentioned in connection with the hypothetical crystal in Part I, the sense of rotation would also depend on the nature of the anisotropy of oxygen in the structure.

Summary

Using the general theory of Part I, the rotatory power of β-quartz along and perpendicular to the axis are calculated to be 236° and 115°. These agree well with the value 252° observed for the former and the value 0·50 observed for the ratio of the two in α-quartz.

References

1. Bhagavantam, S. .. *Scattering of Light and Raman Effect*, Waltair, 1940.
2. Bragg .. *Proc. Roy. Soc.*, **A**, 1924, **105**, 370.
3. ——— and Gibbs .. *Ibid.*, 1925, **109**. 405.
4. Bruhat and Grivet .. *J. de Phys.*, 1935 (7) **6**, 12.
5. Fajans and Joos .. *Zeits. f. Phys.*, 1924, **23**, 1.
6. Ramachandran .. *Proc. Ind. Acad. Sci.*, 1951 *a*, *b*, **33A**, 217, 309.
7. Sosman .. "Properties of Silica," A.C.S. *Monograph Series*, 1927.

THERMO-OPTIC BEHAVIOUR OF SILICON CARBIDE

By A. K. Ramdas

(*From the Raman Research Institute, Bangalore*)

Received July 9, 1951

(Communicated by Sir C. V. Raman, N.L.)

1. Introduction

Silicon carbide (carborundum) is a trigonal crystal which crystallises in thin basal plates. It is colourless when pure, but usually coloured green, blue, or black due to impurities of small amounts of iron, alumina, carbon, etc. It is uniaxial positive with extremely high refraction, strong birefringence and very strong dispersion. The refractive indices of carborundum, both ordinary and extraordinary, has been determined by Weigel (1915) and by Merwin (1917) for the visible region. Weigel has also determined the rate of variation of the ordinary as well as the extraordinary refractive index with temperature over three ranges of temperature and for four wave-lengths. In this paper it is proposed to discuss the thermo-optic behaviour of carborundum, utilising Weigel's data and applying the theory of thermo-optic behaviour of solids due to Dr. G. N. Ramachandran (1947).

2. Derivation of the Dispersion Fourmulæ

The derivation of accurate dispersion formulæ is a necessary step to the theoretical explanation of the thermo-optic behaviour of solids. As the data available cover a limited range, a dispersion formula involving the fewest absorption wave-lengths would seem the most appropriate. In fact, an attempt was made to derive a dispersion formula using only one absorption wave-length of the following type:

$$n_i^2 = 1 + \frac{k\lambda^2}{\lambda^2 - \lambda_1^2}, \; n_i = \omega, \; \epsilon.$$

This was found to fail, as the same dispersion wave-length did not satisfy the formulæ for the ordinary and the extraordinary refractive indices. In other words, a mere change in the oscillator strength is incapable of explaining the birefringence of carborundum with this type of formula. An attempt was therefore made to fit in the data using two frequencies in the dispersion formula, *viz.*, by formulæ of the following type:

$$\omega^2 = 1 + \frac{k_1\lambda^2}{\lambda^2 - \lambda_1^2} + \frac{k_2\lambda^2}{\lambda^2 - \lambda_2^2} \tag{1}$$

$$\epsilon^2 = 1 + \frac{k_3\lambda^2}{\lambda^2 - \lambda_1^2} + \frac{k_4\lambda^2}{\lambda^2 - \lambda_2^2}. \tag{2}$$

The constants are found to be:

$$k_1 = 3{\cdot}657,\ k_2 = 1{\cdot}898,$$
$$k_3 = 1{\cdot}626,\ k_4 = 4{\cdot}110,$$
$$\lambda_1 = 155\ m\mu,\ \lambda_2 = 175\ m\mu.$$

(The wave-lengths are measured in millimicrons.)

In Table I, the calculated and experimental values are compared and the formulæ are seen to agree very well. The agreement of the dispersion formulæ with experimental values justifies the assumption that the dispersion frequencies are the same for the ordinary and the extraordinary indices but that only their strengths alter with the direction of the electric vector.

TABLE I

ω = Ordinary refractive index

λ	ω (obs.)	ω (cal.)	Difference
436	2·7292	2·7292	0·0000
455	2·7138	2·7138	0·0000
492	2·6894	2·6894	0·0000
502	2·6842	2·6838	−0·0004
546	2·6632	2·6632	0·0000
578	2·6513	2·6514	+0·0001
588	2·6481	2·6481	0·0000
668	2·6271	2·6273	+0·0002
706	2·6195	2·6195	0·0000

TABLE II

ϵ = Extraordinary refractive index

λ in $m\mu$	ϵ (obs.)	ϵ (cal.)	Difference
436	2·7859	2·7859	0·0000
455	2·7677	2·7682	+0·0005
492	2·7401	2·7405	+0·0004
502	2·7342	2·7342	0·0000
546	2·7106	2·7109	+0·0003
578	2·6974	2·6974	0·0000
588	2·6939	2·6939	0·0000
668	2·6707	2·6705	−0·0002
706	2·6623	2·6623	0·0000

3. THERMAL VARIATION OF THE REFRACTIVE INDICES

We now apply Ramachandran's theory of thermo-optic behaviour to this case. The theory considers the variation of refractive index with temperature as due to the sum of two effects, one arising from a change of

volume which causes a change in the number of dispersion centres, and the other from a shift in the position of the dispersion wave-lengths. So, differentiating (1) and (2) with respect to temperature t, we get

$$\frac{d\omega}{dt} = -\frac{\gamma}{2\omega}(\omega^2 - 1) + \frac{1}{\omega}\frac{k_1\lambda^4}{(\lambda^2 - \lambda_1^2)^2}\chi_1 + \frac{1}{\omega}\frac{k_2\lambda^4}{(\lambda^2 - \lambda_2^2)^2}\chi_2 \qquad (3)$$

$$\frac{d\epsilon}{dt} = -\frac{\gamma}{2\epsilon}(\epsilon^2 - 1) + \frac{1}{\epsilon}\cdot\frac{k_3\lambda^4}{(\lambda^2 - \lambda_1^2)^2}\chi_1 + \frac{1}{\epsilon}\frac{k_4\lambda^4}{(\lambda^2 - \lambda_2^2)^2}\chi_2, \qquad (4)$$

where γ = coefficient of cubical expansion.

$$\chi_1 = \frac{1}{\lambda_1}\left(\frac{d\lambda_1}{dt}\right),\ \chi_2 = \frac{1}{\lambda_2}\left(\frac{d\lambda_2}{dt}\right).$$

Weigel has determined the temperature variation of the ordinary index for four wave-lengths and three temperature ranges, and the temperature variation of the extraordinary index for two wave-lengths and two temperature ranges. It is found that on making $\chi_1 = \chi_2 = \chi$, the value of χ satisfies the expressions for the variation with temperature of both the ordinary and the extraordinary refractive indices. The value of χ for the temperature range 20°–460° is found to be 35×10^{-6}. The values of χ and the corresponding $\frac{d\omega}{dt}$ and $\frac{d\epsilon}{dt}$ for different temperature ranges are given in Table III along with the experimental values.

TABLE III

Wave-length in $m\mu$	Temp. 20° – 460° C. $\gamma = 18 \times 10^{-6}$ $\chi = 35 \times 10^{-6}$		Temp. 460° – 760° C. $\gamma = 15 \times 10^{-6}$ $\chi = 42 \times 10^{-6}$		Temp. 760° – 1150° C. $\gamma = 13{\cdot}5 \times 10^{-6}$ $\chi = 45 \times 10^{-6}$	
	$\frac{d\omega}{dt} \times 10^5$ calc.	$\frac{d\omega}{dt} \times 10^5$ obs.	$\frac{d\omega}{dt} \times 10^5$ calc.	$\frac{d\omega}{dt} \times 10^5$ obs.	$\frac{d\omega}{dt} \times 10^5$ calc.	$\frac{d\omega}{dt} \times 10^5$ obs.
471	7·2	7·5	9·5	10·0		
554	6·6	6·6	8·6	8·2	9·7	$9{\cdot}7_3$
650	6·4	6·1	8·4	7·6	9·3	$9{\cdot}0_0$
668	6·3	6·9	8·1	7·4		
	$\frac{d\epsilon}{dt} \times 10^5$ calc.	$\frac{d\epsilon}{dt} \times 10^4$ obs.	$\frac{d\epsilon}{dt} \times 10^5$ calc.	$\frac{d\epsilon}{dt} \times 10^5$ obs.		
471	7·5	8·2	10	11·5		
668	6·5	6·3	8·5	8·0		

Table III shows that the theory explains the increase with temperature of both the ordinary and the extraordinary indices. It is seen also that the value of χ increases with temperature. Though the theory gives a decreasing $\frac{d\omega}{dt}$ and $\frac{d\epsilon}{dt}$ for increasing wave-lengths, this decrease is not quite so rapid as that appearing in the experimental data. The explanation of this discrepancy will be discussed presently.

4. Comparison with the Case of Diamond

It is instructive to compare the behaviour of carborundum and diamond. Both substances have similar high refractivities, high dispersion and great hardness, while their structures exhibit a very similar disposition of the valence bonds. The compressibilities of diamond and carborundum are also not very different. The thermal expansion coefficient of carborundum is, however, six times greater than that for diamond, a circumstance which

Table IV

	Refractive index n_D	Hardness on Moh's Scale	Compressibility	Thermal expansion	χ	Principal Infra-red absorption
Diamond ..	2·42	10	$1{\cdot}6 \times 10^{-7}$ per atm.	3×10^{-6}	$7{\cdot}6 \times 10^{-6}$	8μ
Carborumdum	$\omega = 2{\cdot}65$ $\epsilon = 2{\cdot}69$	9·5	$2{\cdot}2 \times 10^{-7}$ per atm.	18×10^{-6}	35×10^{-6}	12μ

is no doubt connected with the notable difference in the vibration frequencies of the respective crystal structures. It will be noticed that the value of χ for carborundum is nearly five times larger than for diamond.

A more detailed comparison brings out some further points of interest. The dispersion formula for diamond is given by Ramachandran as

$$n^2 = 1 + \frac{4{\cdot}337\,\lambda^2}{\lambda^2 - 106^2} + \frac{0{\cdot}3309\,\lambda^2}{\lambda^2 - 175^2}.$$

This may be compared with the formulæ in the case of carborundum given above, *viz.*,

$$\omega^2 = 1 + \frac{3{\cdot}657\,\lambda^2}{\lambda^2 - 155^2} + \frac{1{\cdot}898\,\lambda^2}{\lambda^2 - 175^2}$$

$$\epsilon^2 = 1 + \frac{1{\cdot}626\,\lambda^2}{\lambda^2 - 155^2} + \frac{4{\cdot}11\,\lambda^2}{\lambda^2 - 175^2}.$$

The dispersion data in the case of diamond very clearly indicate a weak electronic absorption wave-length at 175 $m\mu$. The electronic absorptions at 155 $m\mu$ and 175 $m\mu$ in carborundum evidently correspond to the strong

term at 106 $m\mu$ in diamond, the doubling being presumably connected with the anisotropy of structure of the former. Though the available data do not indicate any term or terms for carborundum corresponding to the absorption wave-length at 175 $m\mu$ in diamond, one may reasonably surmise the existence of a term or perhaps two such terms between 200 $m\mu$ to 250 $m\mu$. Such terms would not make a large contribution to the refraction or dispersion, but might nevertheless sensibly influence the temperature coefficient of the refractive indices in the direction of making it decrease more rapidly as the wave-length increases. It is suggested that this may be the origin of the discrepancies between the observed and calculated values appearing in Table III.

In conclusion, I wish sincerely to thank Prof. Sir C. V. Raman, F.R.S., N.L., for suggesting the problem and for his guidance and encouragement.

6. Summary

The dispersion and birefringence of carborundum are well represented by the formulæ

$$\omega^2 = 1 + \frac{k_1 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{k_2 \lambda^2}{\lambda^2 - \lambda_2^2}$$

$$\epsilon^2 = 1 + \frac{k_3 \lambda^2}{\lambda^2 - \lambda_1^2} + \frac{k_4 \lambda^2}{\lambda^2 - \lambda_2^2}, \text{ where}$$

$\lambda_1 = 155\ m\mu$, $\lambda_2 = 175\ m\mu$, $k_1 = 3{\cdot}657$, $k_2 = 1{\cdot}898$, $k_3 = 1{\cdot}626$, $k_4 = 4{\cdot}11$.

The theory of thermo-optic behaviour of solids when applied to the case of carborundum explains the observed positive temperature coefficient of both the indices.

References

1. Merwin .. *Jour. Wash. Acad. Sci.*, 1917, **7** (Quoted in Winchell's *Microscopic Characters of Artificial Minerals*).
2. Ramachandran, G. N. .. *Proc. Ind. Acad. Sci.*, 1947, **25** A, 266.
3. Weigel .. *Nachrichten von der königlichen gesellschaft der Wissenschaften zu Göttingen*, 188, 1915; 264, 299 (quoted in *International Critical Tables*).

499-51. Printed at The Bangalore Press, Mysore Road, Bangalore City, by G. Srinivasa Rao, Superintendent and Published by The Indian Academy of Sciences, Bangalore